PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C07C 22/00, C09K 19/30, 19/40, C07C 25/24, 69/76, 43/192, C07F 7/08

A1

(11) International Publication Number: **WO 97/34855**

(43) International Publication Date: 25 September 1997 (25.09.97)

(21) International Application Number: PCT/JP97/00700

(22) International Filing Date: 6 March 1997 (06.03.97)

(30) Priority Data:
8/90585 18 March 1996 (18.03.96) JP

(71) Applicant *(for all designated States except US)*: CHISSO CORPORATION [JP/JP]; 6-32, Nakanoshima 3-chome, Kita-ku, Osaka-shi, Osaka 530 (JP).

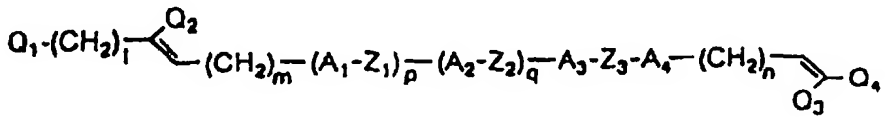
(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: KATO, Takashi [JP/JP]; 27-2, Tatsumidaihigashi 3-chome, Ichihara-shi, Chiba 290 (JP). MATSUI, Shuichi [JP/JP]; 17, Tatsumidaihigashi 2-chome, Ichihara-shi, Chiba 290 (JP). MIYAZAWA, Kazutoshi [JP/JP]; 3-27-7, Chiharadai, Ichihara-shi, Chiba 290-01 (JP). SEKIGUCHI, Yasuko [JP/JP]; 641-1, Matsugashima, Ichihara-shi, Chiba 290 (JP). NAKAGAWA, Etsuo [JP/JP]; 8890, Goi, Ichihara-shi, Chiba 290 (JP).

(74) Agent: NONAKA, Katsuhiko; 4-15, Tsukiji 4-chome, Chuou-ku, Tokyo 104 (JP).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: BISALKENYL DERIVATIVES, LIQUID CRYSTALLINE COMPOUNDS AND LIQUID CRYSTAL COMPOSITIONS



(1)

(57) Abstract

Liquid crystalline compounds expressed by formula (1), liquid crystal compositions thereof obtained by combination with specified liquid crystal compounds, and liquid crystal display devices using them, wherein A_1, A_2, A_3 and A_4 denote each independently trans-1,4-cyclohexylene group etc.; Z_1, Z_2 and Z_3 denote each independently $-(CH_2)_2-$ etc.; Q_1 and Q_2 denote each independently H, F, Cl or Br; Q_3 and Q_4 denote each independently F, Cl or Br; l, m and n denote each independently an integer of from 0 to 5; and p and q denote each independently an integer of 0 or 1.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

DESCRIPTION

Bisalkenyl derivatives, liquid crystalline compounds and liquid crystal compositions

Technical Field

The present invention relates to liquid crystalline compounds and liquid crystal compositions, in more detail novel liquid crystalline compounds having an alkenyl group optionally substituted by halogen and an alkenyl group substituted by halogen simultaneously at both terminals of compounds, liquid crystal compositions containing them, as well as liquid crystal display devices constituted by using the said liquid crystal compositions.

Background Art

There have been many display devices which utilizing a refractive anisotropy and a dielectric anisotropy, characteristics of liquid crystalline compounds. Those display devices are used widely in watches, electronic computers, word processsors, television sets etc., demands of which have been increased year by year. Liquid crystal phase is positioned between solid phase and liquid phase, and liquid crystal phase is classified roughly into nematic phase, smectic phase, and cholesteric phase, and among them, display devicesutilizing nematic phase are most widely used.

Furthermore, as display methods applied for liquid crystal displays, there are present TN (twist nematic) type, DS (dinamic scattering) type, guest-host type and DAP type etc. concerning to their electric optical effects. In particular, colorization of liquid crystal display has been recently more progressed, wherein the main currents are a thin film transistor (TFT) method and a super twist nematic (STN) method concerning to TN type, and these display devices are mass-produced.

Although a number of liquid crystalline compounds including those in study are known, there is not present any substance which is enclosed and used in display devices as a single liquid crystalline substance. The reasons thereof is that there has not been found any substance to satisfy the following conditions as a single substance: namely, that liquid crystalline compounds to be expected as materials of display devices are desired to show a liquid crystal phase within a wide temperature range as possible in nature centering around the room temperature, which is most often used for display devices, that the compounds should be sufficiently stable against environmental factors to be used, and that the compounds should have physical properties sufficient for driving display devices.

Thus, compositions having such characteristics are prepared and used practically by mixing several liquid crystalline compounds or non-liquid crystalline compounds. These liquid crystal compositions are required to be stable against moisture, light, heat, and air etc. which are generally present in the

used environment. In addition, stabilities against electric field and electromagnetic radiation are necessary and also the liquid crystalline compounds mixed are required to be chemically stable each other in the used environment.

Furthermore, liquid crystal compositions are necessary to have suitable values of physical properties such as a refractive anisotropy value (Δn), a dielectric anisotropy value ($\Delta \varepsilon$), a viscosity (η), a conductivity and an elastic constant ratio K_{33}/K_{11} (K_{33}: bend constant, K_{11}: splay elastic constant) etc. according to display methods and device forms. Furthermore, it is important that each components in liquid crystal compositions have good solubilities mutually.

Among these physical property values, particularly a wide liquid crystal phase temperature range, a low viscosity and a high elastic constant ratio K_{33}/K_{11} are required for liquid crystal compounds to be used in a STN type display method. Recently, environments in which display devices being used are divesified so that materials having a wide liquid crystal phase temperature range are necessary from requirements caused by those environments, and a low viscosity is a necessary and indispensable characteristic for attaining a high speed response, and a high elastic constant ratio K_{33}/K_{11} makes a change in a transmittance sharply in vicinity of a threshold voltage and also makes display devices with a high contrast possible.

In general, compounds having (an) alkenyl group(s) are known to show low viscosities. However, when comparing compounds

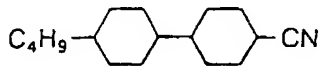
having (an) alkyl group(s) and compounds having (an) alkenyl group(s), compounds having (an) alkenyl group(s) have such tendencies that smectic properties are decreased but liquid crystal phase temperature ranges are also decreased.

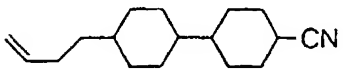
Absolutely, from comparison of compounds (a-1) to (c-2) described in V. Vill, Landort-Velunstein, in bicyclohexyl derivatives (a-1) and (a-2), the clearing point of (a-2) having (an) alkenyl group(s) is about 1 ℃ higher than (a-1) having (an) alkyl group(s), whereas the melting point of the former is about 23℃ higher than the latter. Therefore, the liquid crystal phase temperature range is decreased by about 22℃. The increasing tendencies of the clearing point and theme lting point are found by comparison of cyclohexylphenyl derivatives (b-1) and (b-2), wherein the liquid crystal phase temperature range is decreased by about 10℃.

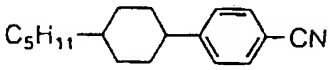
Furthermore, in biphenyl derivatives (c-1) and (c-2), liquid crystal phase temperature ranges are decreased by about 37℃ owing to decrease in the clearing point and increase in the melting point. In both cases, the liquid crystal phase temperature ranges are eminently decreased by substituting an alkyl group with an alkenyl group.

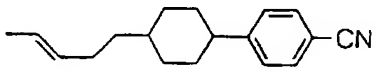
Furthermore, as to compounds showing a high elastic constant ratio K_{33}/K_{11}, there have been already known compounds having (an) alkenyl group(s) in side chains such as compound (d) described in Toku-Ko-Hei 4-30382 or compound (e) described in Toku-Ko-Hei 7-2653. These compounds have however poor appearances of liquid crystal phases, and temperature ranges

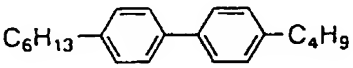
thereof are very narrow even if appearances are obtained. Thus, in the case that they are used as components of liquid crystal compositions, deposition of crystals or appearance of smectic phase may be confirmed at a lower temperature range so that solubility at a lower temperature cannot be said good.

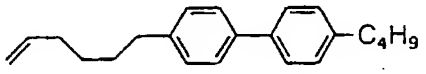
(a-1)  C 28 S 54 N 79 I

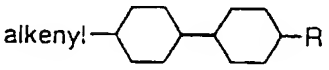
(a-2)  C 50.7 N 79.8 I

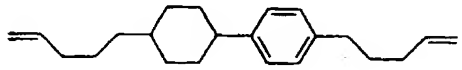
(b-1)  C 31 N 55 I

(b-2)  C 59.8 N 73.7 I

(c-1)  C -2 S_E 40.5 S_B 48.5 I

(c-2)  C 24.4 S_B 38.5 I

(d) 

(e) 

Problems to be solved by the Invention

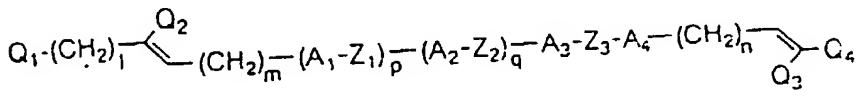
An object of the invention is to propose liquid crystalline compounds, liquid crystal compositions containing them and liquid crystal display devices constituted by using the said liquid crystal compositions, wherein a liquid crystal phase

temperature range being particularly wide, a viscosity being low, an elastic constant ratio K_{33}/K_{11} being high and a solubility at a lower temperature being improved, in order to solve problems of conventional methods.

Disclosure of Invention

Inventions to be claimed in the present application are as follows.

(1) A liquid crystalline compound expressed by the general formula (1)



(1)

wherein, A_1, A_2, A_3 and A_4 denote each independently trans-1,4-cyclohexylene group, trans-1,4-silacyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on 6-membered ring(s) are optionaly substituted with (a) halogen atom(s), pyrimidine-2,5-diyl group, 1,3-dioxane-2,5-diyl group, tetrahydropyran-2,5-diyl group, 1,3-dithiane-2,5-diyl group or tetrahydrothiopyran-2,5-diyl group; Z_1, Z_2 and Z_3 denote each independently $-(CH_2)_2-$, $-(CH_2)_4-$, -CH=CH-, -C≡C-, -COO-, -OCO-, $-CH_2O-$, $-OCH_2-$, -CF=CF- or a covalent bond; Q_1 and Q_2 denote each independently H, F, Cl, Br or an alkenyl group having 2 to 5 carbon atoms; Q_3 and Q_4 denote each independently H, F, Cl or Br; l, m and n denote each independently an integer of 0 to 5; and p and q denote each independently an integer of 0 or 1.

(2) A liquid crystalline compound according to the above-mentioned (1), wherein p, q and n are 0; Q_3 and Q_4 are F; Z_3 is a covalent bond; and A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

(3) A liquid crystalline compound according to above-mentioned (1), wherein p and q are 0; Q_3 and Q_4 are F; Z_3 is a covalent bond; and A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

(4) A liquid crystalline compound according to above-mentioned (1), wherein p and n are 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; and A_2, A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

(5) A liquid crystalline compound according to above-mentioned (1), wherein p is 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; and A_2, A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

(6) A liquid crystalline compound according to above-mentioned (1), wherein p and n are 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; A_2 is 1, 4-phenylene group; and A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

(7) A liquid crystalline compound according to above-mentioned (1), wherein p is 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; A_2 is 1, 4-phenylene group; and A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

(8) A liquid crystalline compound according to above-mentioned (1), wherein p and n are 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; A_2 and A_3 are 1, 4-phenylene groups, and A_4

is trans-1,4-cyclohexylene group in the general formula (1).

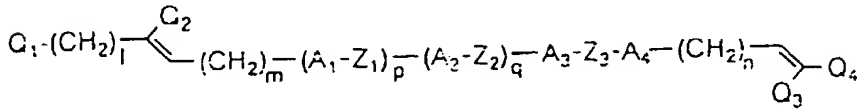
(9) A liquid crystalline compound according to above-mentioned (1), wherein p is 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; A_2 and A_3 are 1, 4-phenylene groups; and A_4 is trans-1,4-cyclohexylene group in the general formula (1).

(10) A liquid crystalline compound according to above-mentioned (1), wherein p and q are 1; n is 0; Q_3 and Q_4 are F; Z_1, Z_2 and Z_3 are covalent bonds; A_1 and A_4 are trans-1,4-cyclohexylene groups; and A_2 and A_3 are 1,4-phenylene groups in the general formula (1).

(11) A liquid crystalline compound according to above-mentioned (1), wherein p and q are 1; Q_3 and Q_4 are F; Z_1, Z_2 and Z_3 are covalent bonds; A_1 and A_4 are trans-1,4-cyclohexylene groups, and A_2 and A_3 are 1, 4-phenylene groups in the general formula (1).

(12) A liquid crystal composition consisting of two or more than two components and a display device using the said composition, wherein at least one liquid compound(s) according to any of above-mentioned (1) to (11) is(are) contained.

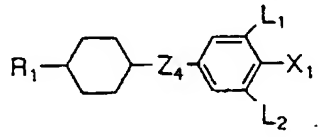
(13) A liquid crystal composition characterized in that at least one liquid crystalline compound(s) expressed by the general formula (1)



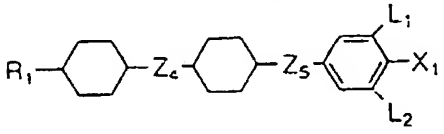
(1)

wherein, A_1, A_2, A_3 and A_4 denote each independently trans-1,4-cyclohexylene group, trans-1,4-silacyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on 6-membered ring(s) are optionaly substituted with (a) halogen atom(s), pyrimidine-2,5-diyl group, 1,3-dioxane-2,5-diyl group, tetrahydropyran-2,5-diyl group, 1,3-dithiane-2,5-diyl group or tetrahydrothiopyran-2,5-diyl group; Z_1, Z_2 and Z_3 denote each independently $-(CH_2)_2-$, $-(CH_2)_4-$, $-CH=CH-$, $-C\equiv C-$, $-COO-$, $-OCO-$, $-CH_2O-$, $-OCH_2-$, $-CF=CF-$ or a covalent bond; Q_1 and Q_2 denote each independently H, F, Cl, Br or an alkenyl group having 2 to 5 carbon atoms; Q_3 and Q_4 denote each independently H, F, Cl or Br; l, m and n denote each independently an integer of 0 to 5; and p and q denote each independently an integer of 0 or 1, is(are) contained as the first component, and

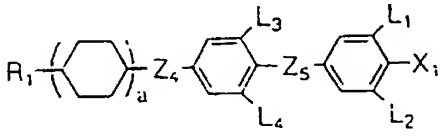
that at least one compound(s) selected from the group consisting of the general formulae (2), (3) and (4)



(2)



(3)



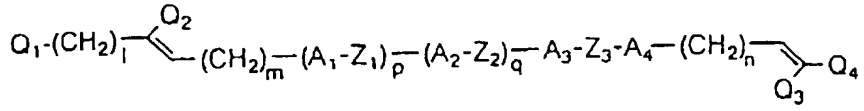
(4)

wherein, R_1 denotes an alkyl group having 1 to 10 carbon atoms; X: denotes F, Cl, OCF_3, OCF_2H, CF_3, CF_2H or CFH_2; L_1, L_2, L_3 and L_4 denote each independently H or F; Z_4 and Z_5 denote each

independently $-(CH_2)_2-$, -CH=CH- or a covalent bond; and a denotes 1 or 2,

is(are) contained as the second component.

(14) A liquid crystal composition characterized in that at least one liquid crystalline compound(s) expressed by the general formula (1)

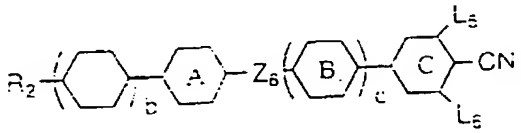


(1)

wherein, A_1, A_2, A_3 and A_4 denote each independently trans-1,4-cyclohexylene group, trans-1,4-silacyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on 6-membered ring(s) are optionaly substituted with (a) halogen atom(s), pyrimidine-2,5-diyl group, 1,3-dioxane-2,5-diyl group, tetrahydropyran-2,5-diyl group, 1,3-dithiane-2,5-diyl group or tetrahydrothiopyran-2,5-diyl group; Z_1, Z_2 and Z_3 denote each independently $-(CH_2)_2-$, $-(CH_2)_4-$, -CH=CH-, $-C\equiv C-$, -COO-, -OCO-, $-CH_2O-$, $-OCH_2-$, -CF=CF- or a covalent bond; Q_1 and Q_2 denote each independently H, F, Cl, Br or an alkenyl group having 2 to 5 carbon atoms; Q_3 and Q_4 denote each independently H, F, Cl or Br; l, m and n denote each independently an integer of 0 to 5; and p and q denote each independently an integer of 0 or 1,

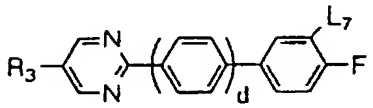
is(are) contained as the first component, and

that at least one compound(s) selected from the group consisting of the general formulae (5), (6), (7), (8) and (9)



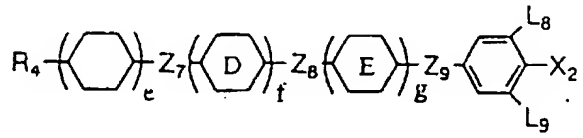
(5)

wherein, R_2 denotes F, an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in the said alkyl group or alkenyl group may be substituted with (an) oxygen atom(s) (-O-) but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring A denotes trans-1,4-cyclohexylene group, 1,4-phenylene group, pyrimidine-2,5-diyl group or 1,3-dioxane-2,5-diyl group; ring B denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring C denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_6 denotes $-(CH_2)_2-$, -COO- or a covalent bond; L_5 and L_6 denote each independently H or F; and b and c denote each independently 0 or 1,



(6)

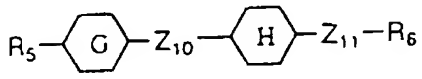
wherein, R_3 denotes an alkyl group having 1 to 10 carbon atoms; L_7 denotes H or F; and d denotes 0 or 1,



(7)

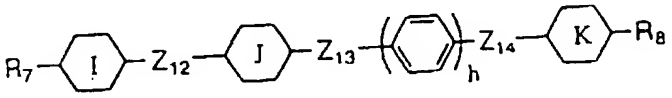
wherein, R_4 denotes an alkyl group having 1 to 10 carbon atoms; ring D and ring E denote each independently trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_7 and Z_8 denote each independently -COO- or a covalent bond; Z_9 denotes -COO- or

$-C\equiv C-$; L_8 and L_9 denote each independently H or F; X_2 denotes F, OCF_3, OCF_2H, CF_3, CF_2H or CFH_2; and e, f and g denote each independently 0 or 1,



(8)

wherein, R_5 and R_6 denote each independently an alkyl group having 1 to 10 carbon atom(s) or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in either cases may be substituted with (an) oxygen atom(s) (-O-) but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring G denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring H denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_{10} denotes $-C\equiv C-$, -COO-, $-(CH_2)_2-$, $-CH=CH-C\equiv C-$ or a covalent bond; and Z_{11} denotes -COO- or a covalent bond,



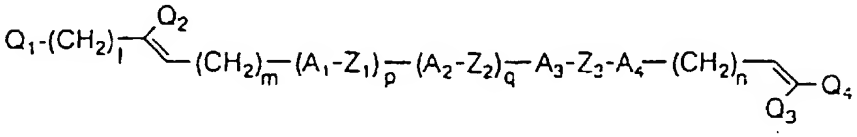
(9)

wherein, R_7 and R_8 denote each independently an alkyl group having 1 to 10 carbon atom(s) or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in either cases may be substituted with (an) oxygen atom(s) (-O-) but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring I denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring J denotes trans-1,4-cyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s)

on ring may be substituted with F, or pyrimidine-2,5-diyl group; ring K denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_{12} and Z_{14} denote each independently -COO-, $-(CH_2)_2-$ or a covalent bond; Z_{13} denotes -CH=CH-, -C≡C-, -COO- or a covalent bond; and h denotes 0 or 1,

is(are) contained as the second component.

(15) A liquid crystal composition and a liquid crystal display device using the said comosition characterized in that at least one liquid crystalline compound(s) expressed by the general formula (1)

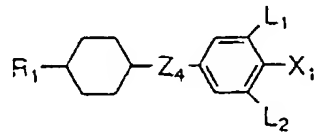


(1)

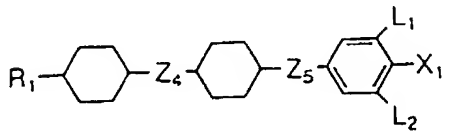
wherein, A_1, A_2, A_3 and A_4 denote each independently trans-1,4-cyclohexylene group, trans-1,4-silacyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on 6-membered ring(s) are optionaly substituted with (a) halogen atom(s), pyrimidine-2,5-diyl group, 1,3-dioxane-2,5-diyl group, tetrahydropyran-2,5-diyl group, 1,3-dithiane-2,5-diyl group or tetrahydrothiopyran-2,5-diyl group; Z_1, Z_2 and Z_3 denote each independently $-(CH_2)_2-$, $-(CH_2)_4-$, -CH=CH-, -C≡C-, -COO-, -OCO-, $-CH_2O-$, $-OCH_2-$, -CF=CF- or a covalent bond; Q_1 and Q_2 denote each independently H, F, Cl, Br or an alkenyl group having 2 to 5 carbon atoms; Q_3 and Q_4 denote each independently H, F, Cl or Br; l, m and n denote each independently an integer of 0 to 5; and p and q denote each independently an integer of 0 or 1,

is(are) contained as the first component,

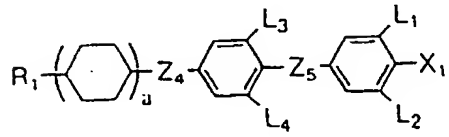
that at least one compound(s) selected from the group consisting of the general formulae (2), (3) and (4)



(2)



(3)

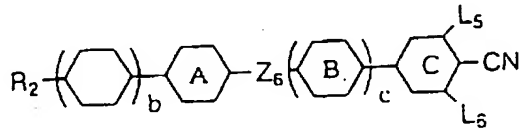


(4)

wherein, R_1 denotes an alkyl group having 1 to 10 carbon atoms; X_1 denotes F, Cl, OCF_3, OCF_2H, CF_3, CF_2H or CFH_2; L_1, L_2, L_3 and L_4 denote each independently H or F; Z_4 and Z_5 denote each independently $-(CH_2)_2-$, -CH=CH- or a covalent bond; and a denotes 1 or 2,

is(are) contained as one part of the second component, and

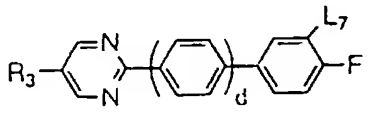
that at least one compound(s) selected from the group consisting of the general formulae (5), (6), (7), (8) and (9)



(5)

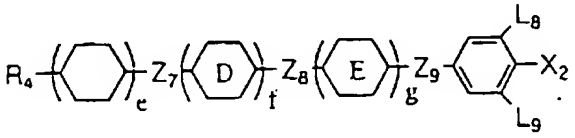
wherein, R_2 denotes F, an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in the said alkyl group or alkenyl group may be substituted with (an) oxygen atom(s) (-O-)

but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring A denotes trans-1,4-cyclohexylene group, 1,4-phenylene group, pyrimidine-2,5-diyl group or 1,3-dioxane-2,5-diyl group; ring B denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring C denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_6 denotes $-(CH_2)_2-$, -COO- or a covalent bond; L_5 and L_6 denote each independently H or F; and b and c denote each independently 0 or 1,



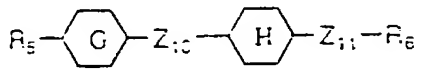
(6)

wherein, R_3 denotes an alkyl group having 1 to 10 carbon atoms; L_7 denotes H or F; and d denotes 0 or 1,



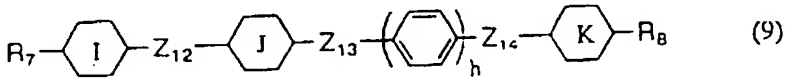
(7)

wherein, R_4 denotes an alkyl group having 1 to 10 carbon atoms; ring D and ring E denote each independently trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_7 and Z_8 denote each independently -COO- or a covalent bond; Z_9 denotes -COO- or $-C\equiv C-$; L_8 and L_9 denote each independently H or F; X_2 denotes F, OCF_3, OCF_2H, CF_3, CF_2H or CFH_2; and e, f and g denote each independently 0 or 1,



(8)

wherein, R_5 and R_6 denote each independently an alkyl group having 1 to 10 carbon atom(s) or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in either cases may be substituted with (an) oxygen atom(s) (-O-) but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring G denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring H denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_{10} denotes $-C\equiv C-$, -COO-, $-(CH_2)_2-$, $-CH=CH-C\equiv C-$ or a covalent bond; and Z_{11} denotes -COO- or a covalent bond,



(9)

wherein, R_7 and R_8 denote each independently an alkyl group having 1 to 10 carbon atom(s) or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in either cases may be substituted with (an) oxygen atom(s) (-O-) but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring I denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring J denotes trans-1,4-cyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on ring may be substituted with F, or pyrimidine-2,5-diyl group; ring K denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_{12} and Z_{14} denote each independently -COO-, $-(CH_2)_2-$ or a covalent bond; Z_{13} denotes $-CH=CH-$, $-C\equiv C-$, -COO- or a covalent bond; and h denotes 0 or 1,

is(are) contained as the second component.

Best Mode for Carrying Out the Invention

Liquid crystalline compounds expressed by the general formula (1) according to the invention are characterized in that they are bicyclic to tetracyclic type derivatives having an alkenyl group substituted by (a) halogen atom(s) and an alkenyl group as substituents on both terminals of molecule. These liquid crystalline compounds are stable physically and chemically under conditions in which display devices being used, and in addition they are characterized to have a wide liquid crystal phase temperature range, a good solubility into liquid crystal compositions even at a lower temperature, a low viscosity and a high elastic constant ratio K_{33}/K_{11}. Furthermore, desired physical properties can be optionally adjusted by selecting adequately ring structures, bonding groups or sutructures of side chains among molecular constitutional factors. Thus, in the case that the compounds of the invention being used as components of liquid crystal compositions, they show good characteristics, in more detail,

1) They have wide liquid crystal phase temperature range in spite of containing alkenyl group.

2) There are obtained decrease in a threshold voltage and improvement in a response speed due to a low viscosity.

3) Nematic liquid crystal composition can be prepared without any deposition of crystals and any appearance of a smectic phase at an extremely low temperature.

4) A high contrast can be obtained due to improvement in an elastic constant ratio K_{33}/K_{11}.

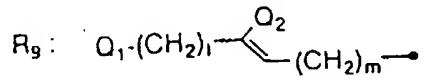
As well as, they are stable against external enveironments and also they can provide novel liquid crystal compositions and liquid crystal display devices by which enlargement of the used temperature range, a driving property at low voltage, a high speed response and a high contrast can be realized.

Compounds having an alkenyl group substituted by (a) halogen(s) independently as a molecular terminal group are disclosed already in Toku-Kai-Hei 1-175947 and Toku-Kai-Hei 1-308239 etc. These compounds are however have strong appearances of smectic phases and narrow liquid crystal phase temperature ranges. Furthermore, elastic constant ratios K_{33}/K_{11} cannot be mentioned to be high. Although it is needless to say that the compounds of the invention all show preferable physical properties, liquid crystal compositions according to objects can be prepared by using compounds of the formula (1) in which A_1, A_2, A_3, A_4, Z_1, Z_2, Z_3, Q_1, Q_2, Q_3, Q_4, l, m, n, p and q are adequately selected.

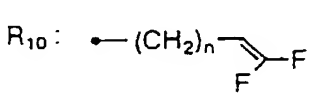
That is, in the case for use in liquid crystal compositions in which a temperature range to appear liquid crystal phase being higher side of the temparature range, tetracyclic type compounds wherein p=q=1 may be used, and in other cases, bicyclic type or tricyclic type compounds may be used, and in particular, in the case of compounds with a low viscosity being necessary, bicyclic type compounds wherein A_3 and A_4 are trans-1,4-cyclohexylene groups may be used. Furthermore, those with fluorine substituted on 1,4-phenylene group show particularly superior solubility at a lower temperature.

Furthermore, if an appropriate refractive anisotropy value being necessary, those wherein A_1, A_2, A_3 and A_4 are 1,4-phenylene groups, and Z_1, Z_2 and Z_3 are covalent bonds may be selected adequately.

Hereinbelow, R_9 is a group shown as follows:



Hereinbelow, R_{10} is a group shown as follows:



Cyc mentioned later denotes trans-1,4-cyclohexylene group, Phe denotes 1,4-phenylene group in which one or more than one hydrogen atom(s) on six-membered rings may be substituted by (a) halogen atom(s), and compounds of the general formula (1) according to the invention are classified as follows.

Compounds having two six-membered rings

R_9-A_3-A_4-R_{10} (1a)

R_9-A_3-Z_3-A_4-R_{10} (1b)

Compounds having three six-membered rings

R_9-A_2-A_3-A_4-R_{10} (1c)

R_9-A_2-Z_2-A_3-A_4-R_{10} (1d)

R_9-A_2-A_3-Z_3-A_4-R_{10} (1e)

R_9-A_2-Z_2-A_3-Z_3-A_4-R_{10} (1f)

Compounds having four six-membered rings

R_9-A_1-A_2-A_3-A_4-R10 (1g)

R_9-A_1-Z_1-A_2-A_3-A_4-R_{10} (1h)

R_9-A_1-A_2-Z_2-A_3-A_4-R_{10} (1i)

R_9-A_1-A_2-A_3-Z_3-A_4-R_{10} (1j)

R_9-A_1-Z_1-A_2-Z_2-A_3-A_4-R_{10} (1k)

R_9-A_1-Z_1-A_2-A_3-Z_3-A_4-R_{10} (1l)

R_9-A_1-A_2-Z_2-A_3-Z_3-A_4-R_{10} (1m)

R_9-A_1-Z_1-A_2-Z_2-A_3-Z_3-A_4-R_{10} (1n)

Among these compounds, compounds expressed by the formulae (1a), (1c) and (1g) are particularly prefarable for attaining objects of the invention.

Compounds expressed by the formula (1a) are classified still more into compounds expressed by the following formulae (1aa) to (1ac).

R_9-Cyc-Cyc-R_{10} (1aa)

R_9-Phe-Cyc-R_{10} (1ab)

R_9-Phe-Phe-R_{10} (1ac)

Among these compouds, compounds expressed by the formulae (1aa) and (1ab) are particularly prefarable. These bicyclic type comopunds show wide liquid crystal phase temperature ranges, eminently low viscosities and high elastic constant ratios K_{33}/K_{11}, as well as they can lower only viscosities eminently without lowering clearing points in the case for use in liquid crystal compositions.

Furthermore, compounds expressed by the formula (1c) are classified still more into compounds expressed by the following formulae (1ca) to (1cd).

R_9-Cyc-Cyc-Cyc-R_{10} (1ca)

R_9-Phe-Cyc-Cyc-R_{10} (1cb)

R_9-Phe-Phe-Cyc-R_{10} (1cc)

R_9-Phe-Phe-Phe-R_{10} (1cd)

Among these compounds, compounds expressed by the formulae (1ca), (1cb) and (1cc) are particularly prefarable. Althogh these tricyclic type compounds also show similar properties as bicyclic type compounds, they can set higher clearing points in the case of use in liquid crystal compositions.

Furthermore, compounds expressed by the formula (1g) are classified still more into compounds expressed by the following formulae (1ga) to (1gc).

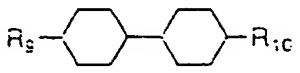
R_9-Cyc-Cyc-Cyc-Cyc-R_{10} (1ga)

R_9-Cyc-Phe-Phe-Cyc-R_{10} (1gb)

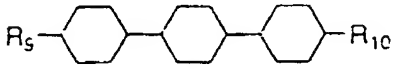
R_9-Cyc-Phe-Phe-Phe-R_{10} (1gc)

Among these compounds, compounds expressed by the formula (1gb) are particularly prefarable. These tetracyclic type compounds have not only high clearing points but also relatively low viscosities, and also they can increase only clearing point with maintaining viscosities in the case for use in liquid crystal compositions.

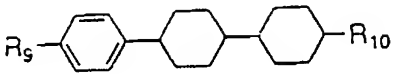
As described above, compounds expressed by the formulae (1aa), (1ab), (1ca), (1cb), (1cc) and (1gb) are particularly preferable examples, and among them, compounds expressed by the following formulae (1-1) to (1-5) are mentioned as more preferable ones.

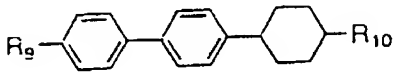


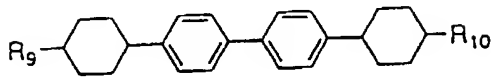
(1-1)



(1-2)


(1-3)


(1-4)


(1-5)

In all compounds described above, R_9 is an alkenyl group having 2 to 12 carbon atoms in which (an) optional H atom(s) may be substituted by F atom(s), and among them, the followings are particularly preferable: vinyl, 1-propenyl, 2-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1,5-hexadienyl, 2-fluoroethenyl, 3-fluoro-1-propenyl, 3-fluoro-2-propenyl, 4-fluoro-1-butenyl, 4-fluoro-2-butenyl, 4-fluoro-3-butenyl, 5-fluoro-1-pentenyl, 5-fluoro-2-pentenyl, 5-fluoro-3-pentenyl, 5-fluoro-4-pentenyl, 2,2-difluoroethenyl, 3,3-difluoro-2-propenyl, 4,4-difluoro-3-butenyl, 5,5-difluoro-4-pentenyl and 6,6-difluoro-5-hexenyl.

Furthermore, R_{10} is a difluoroalkenyl group having 2 to 7 carbon atoms in which (an) optional F atom(s) may be substituted by Cl atom(s), and among them, the followings are particularly preferable: 2,2-difluoroethenyl, 3,3-difluoro-2-propenyl, 4,4-difluoro-3-butenyl, 5,5-difluoro-4-pentenyl, 6,6-difluoro-5-hexenyl, 7,7-difluoro-6-heptenyl, 2-chloro-2-fluoroethenyl, 3-chloro-3-fluoro-2-propenyl, 4-chloro-4-fluoro-3-butenyl, 5-

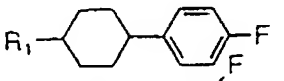
chloro-5-fluoro-4-pentenyl, 6-chloro-6-fluoro-5-hexenyl and 7-chloro-7-fluoro-6-heptenyl.

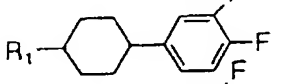
Liquid crystal compositions according to the invention preferably contain one or more than one compound(s) expressed by (1) in a proportion of 0.1 to 99.9% by weight, in order to show superior properties.

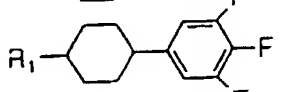
In more detail, liquid crystal compositions provided by the invention are accomplished by mixing the first component which contains at least one compound(s) (1) with (an) optional compound(s) selected from other compound groups or those of the general formulae (2) to (9), according to objects of the liquid crystal compositions.

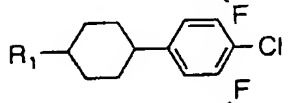
Although liquid crystal compositions provided by the invention may be consisted of the first component which contains at least one liquid crystalline compound(s) shown by the general formula (1), those obtained by mixing the component with at least one component(s) (hereinafter referred to the second A component) selected from the above-mentioned general formulae (2), (3) and (4) and/or at least one component(s) (hereinafter referred to the second B component) selected from the above-mentioned general formulae (5), (6), (7), (8) and (9) as the second components, and also (a) known compound(s) may be mixed in as the third component with the intention of adjusting a threshold voltage, a liquid crystal phase temperature range, a refractive anisotropy value, a dielectric anisotropy value and a viscosity etc.

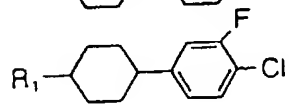
Among the above-mentioned second A components, there may be mentioned (2-1) to (2-15), (3-1) to (3-48) and (4-1) to (4-55) as preferable examples of compounds of the general formulae (2), (3) and (4), respectively.

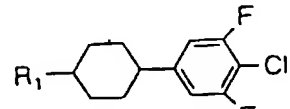

(2-1)

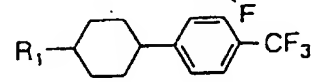

(2-2)

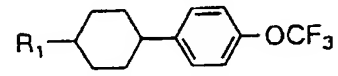

(2-3)

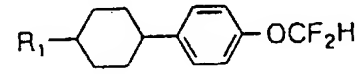

(2-4)

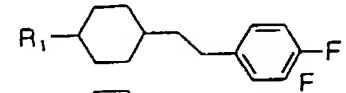

(2-5)

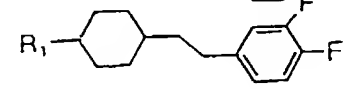

(2-6)

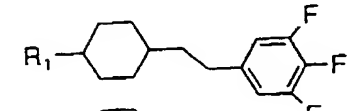

(2-7)

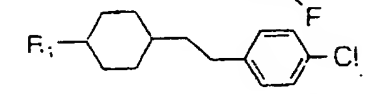

(2-8)

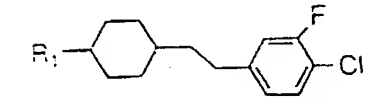

(2-9)

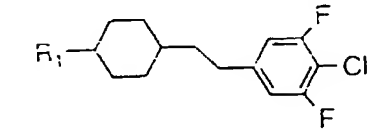

(2-10)

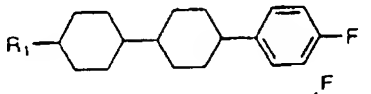

(2-11)

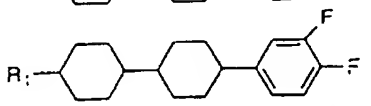

(2-12)

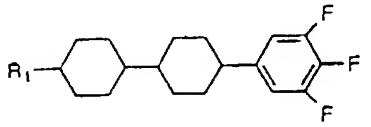

(2-13)

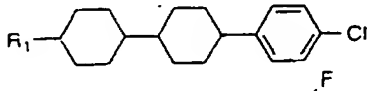

(2-14)

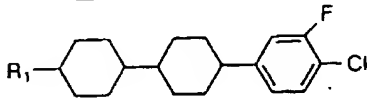

(2-15)

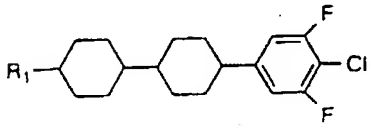

(3-1)

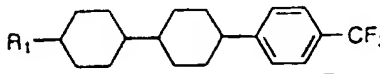

(3-2)

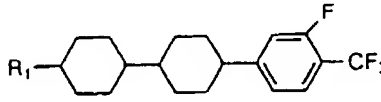

(3-3)

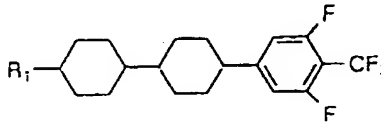

(3-4)

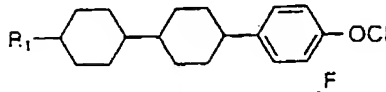

(3-5)

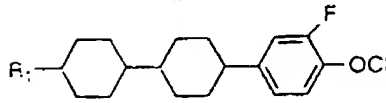

(3-6)

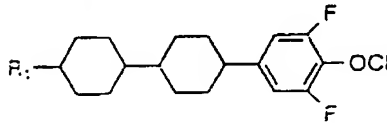

(3-7)

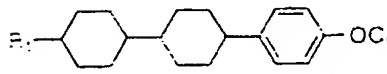

(3-8)

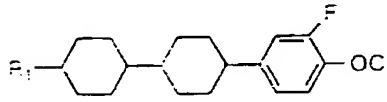

(3-9)

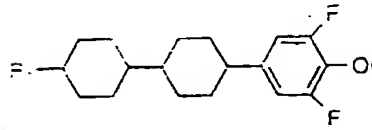

(3-10)

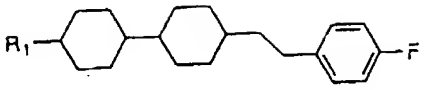

(3-11)

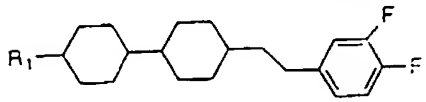

(3-12)

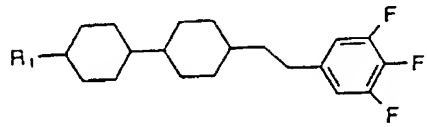

(3-13)

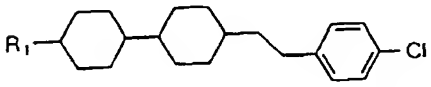

(3-14)

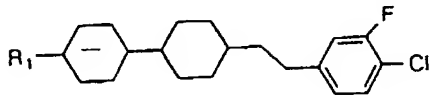

(3-15)

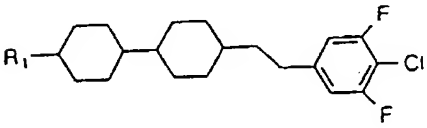

(3-16)

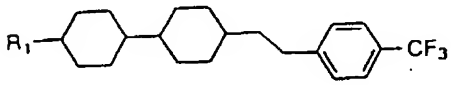

(3-17)

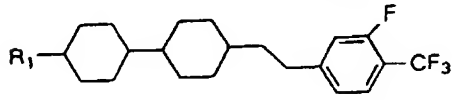

(3-18)

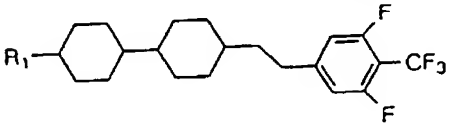

(3-19)

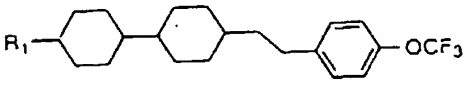

(3-20)

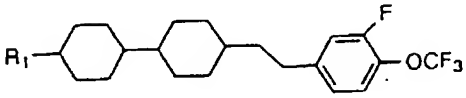

(3-21)

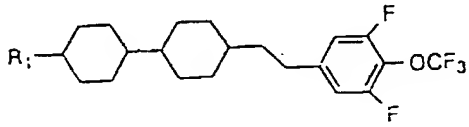

(3-22)

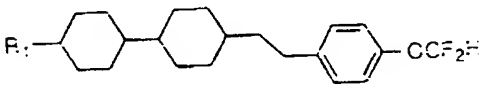

(3-23)

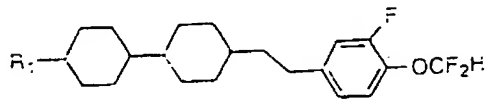

(3-24)

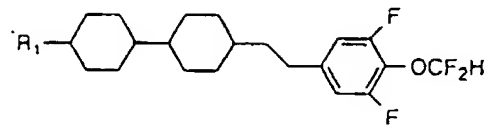

(3-25)

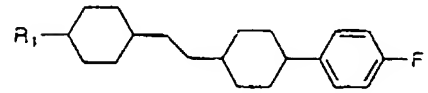

(3-26)

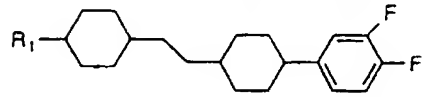

(3-27)

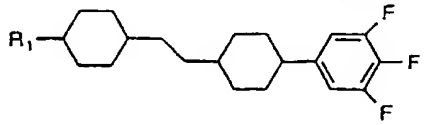

(3-28)

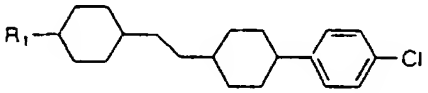

(3-29)

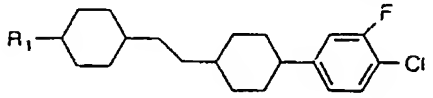

(3-30)

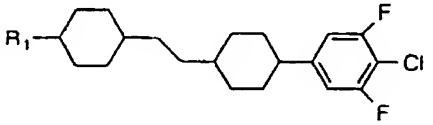

(3-31)

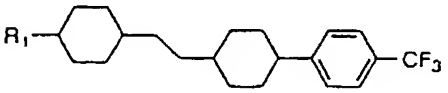

(3-32)

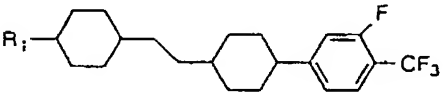

(3-33)

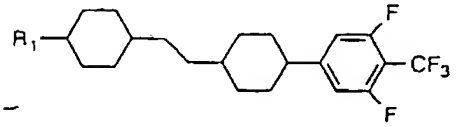

(3-34)

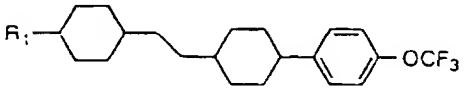

(3-35)

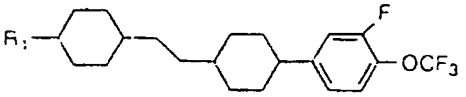

(3-36)

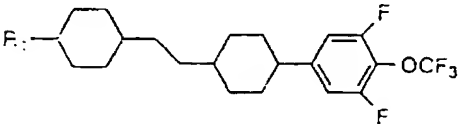

(3-37)

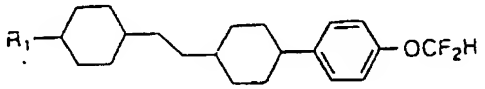

(3-38)

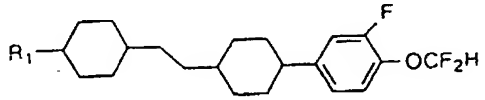

(3-39)

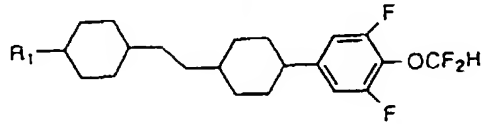

(3-40)

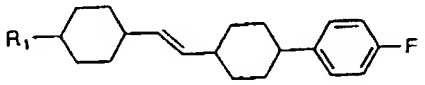

(3-41)

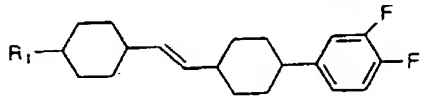

(3-42)

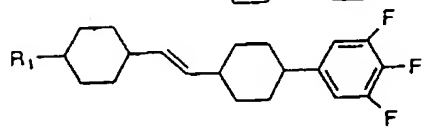

(3-43)

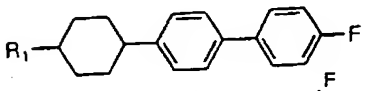

(3-44)

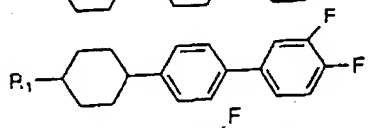

(3-45)

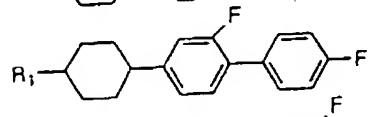

(3-46)

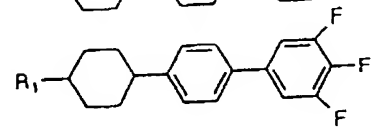

(3-47)

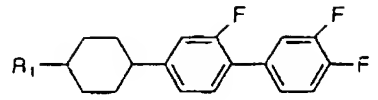

(3-48)

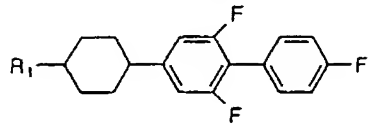

(4-1)

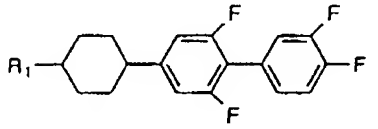

(4-2)

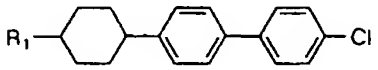

(4-3)

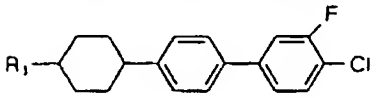

(4-4)

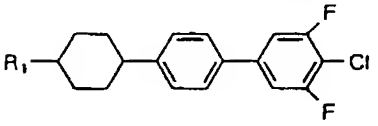

(4-5)

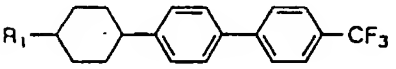

(4-6)

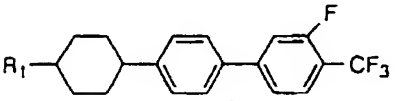

(4-7)

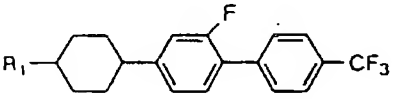

(4-8)

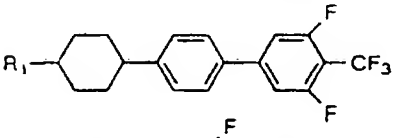

(4-9)

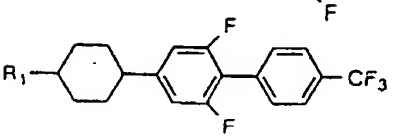

(4-10)

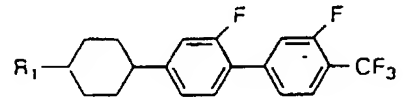

(4-11)

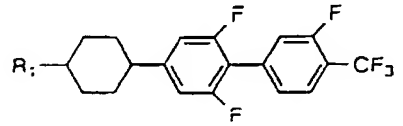

(4-12)

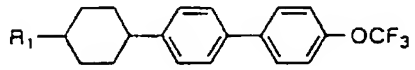

(4-13)

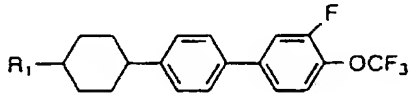

(4-14)

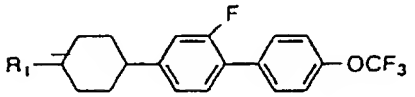

(4-15)

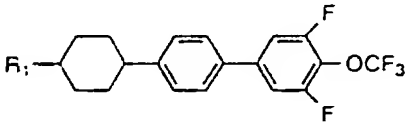

(4-16)

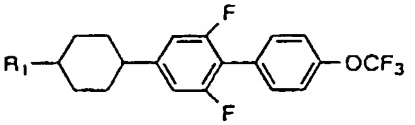

(4-17)

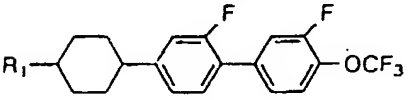

(4-18)

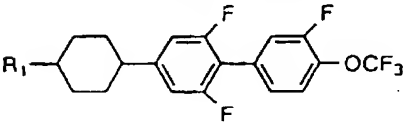

(4-19)

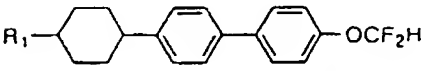

(4-20)

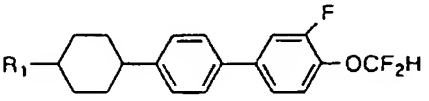

(4-21)

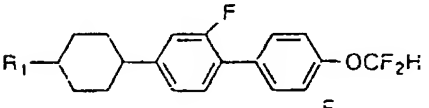

(4-22)

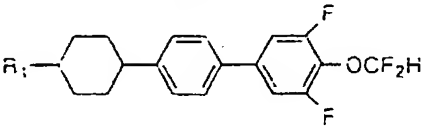

(4-23)

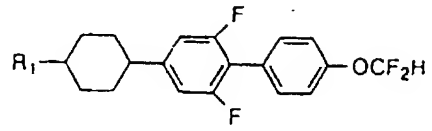

(4-24)

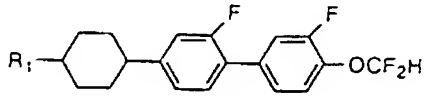

(4-25)

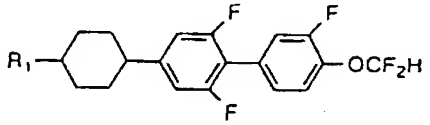

(4-26)

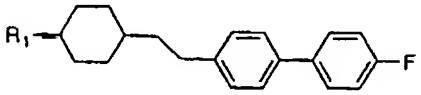

(4-27)

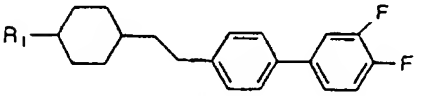

(4-28)

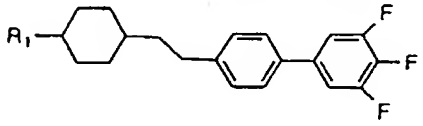

(4-29)

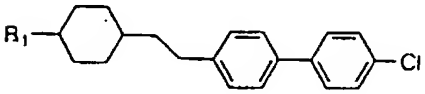

(4-30)

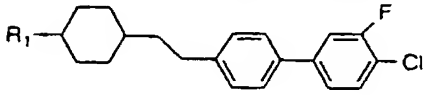

(4-31)

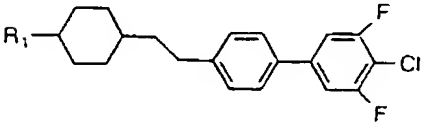

(4-32)

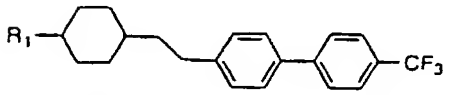

(4-33)

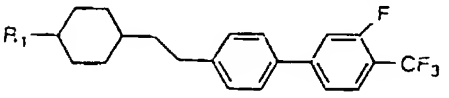

(4-34)

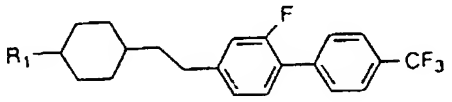

(4-35)

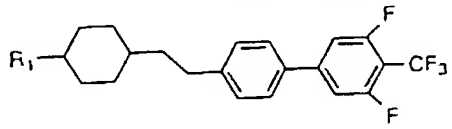

(4-36)

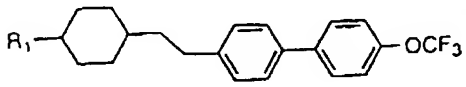

(4-37)

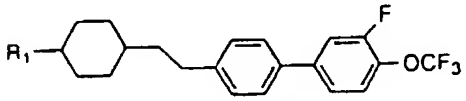

(4-38)

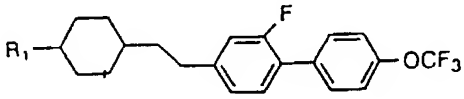

(4-39)

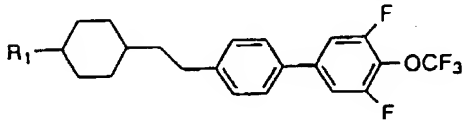

(4-40)

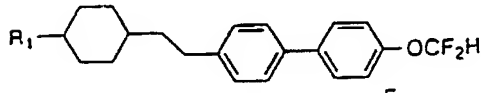

(4-41)

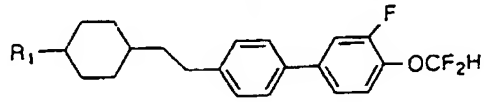

(4-42)

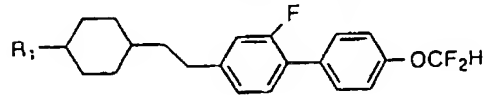

(4-43)

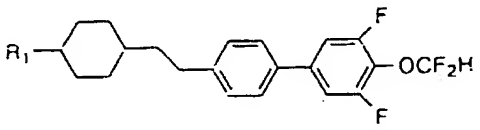

(4-44)

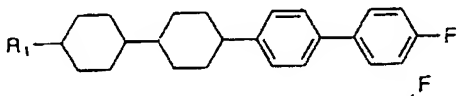

(4-45)

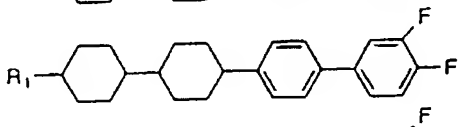

(4-46)

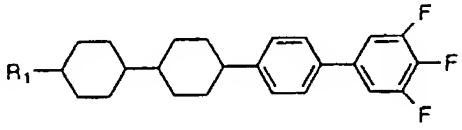

(4-47)

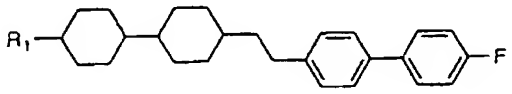

(4-48)

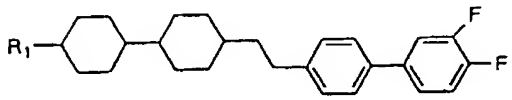

(4-49)

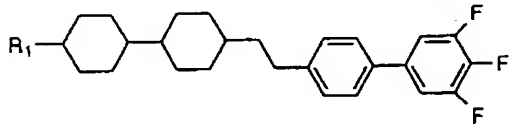

(4-50)


(4-51)


(4-52)


(4-53)


(4-54)

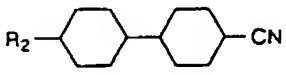

(4-55)

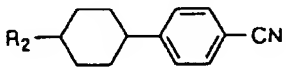
wherein, R_1 denotes the same meaning as the above-mentioned one.

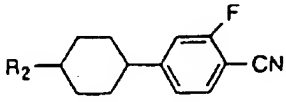
Compounds expressed by these general formulae (2) to (4) show positive dielectric anisotropies and they are very superior in heat stability and chemical stability.

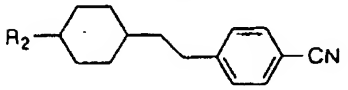
An amount of the said compound used is adequately within a range of 1 to 99% by weight, preferably 10 to 97% by weight, and more preferably 40 to 95% by weight, based on the total weight of a liquid crystal composition.

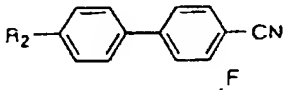
Next, among the above-mentioned second B components, there may be mentioned (5-1) to (5-24), (6-1) to (6-3) and (7-1) to (7-28) as preferable examples of compounds of the general formulae (5), (6) and (7), respectively.

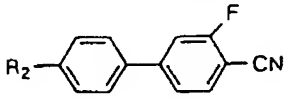

(5-1)

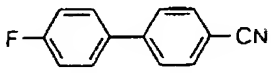

(5-2)

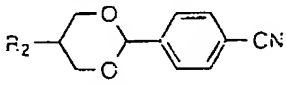

(5-3)

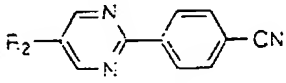

(5-4)

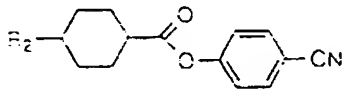

(5-5)

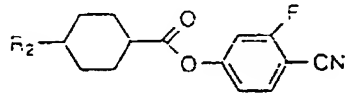

(5-6)

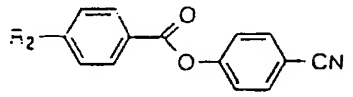

(5-7)

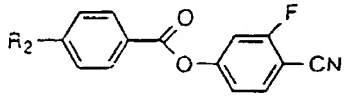

(5-8)

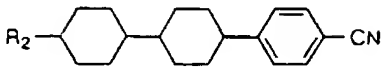

(5-9)

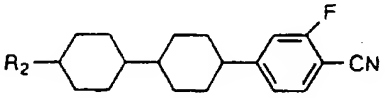

(5-10)

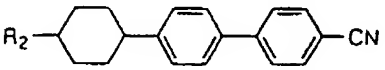

(5-11)

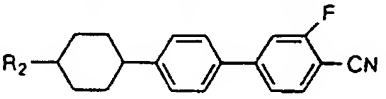

(5-12)

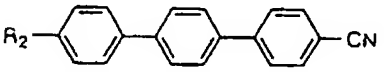

(5-13)

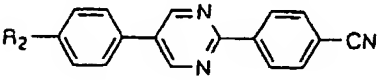

(5-14)

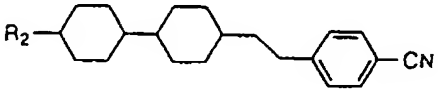

(5-15)

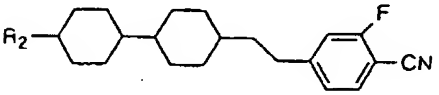

(5-16)

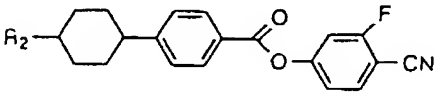

(5-17)

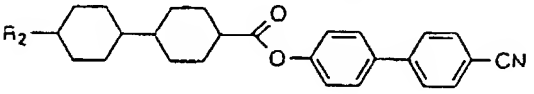

(5-18)

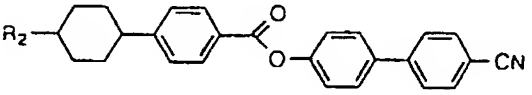

(5-19)

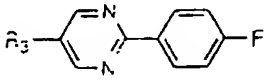

(5-20)

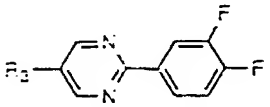

(5-21)

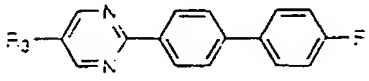

(5-22)

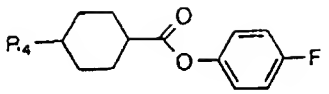

(5-23)

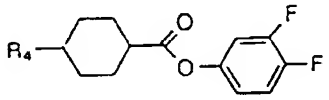

(5-24)

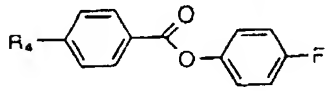

(6-1)

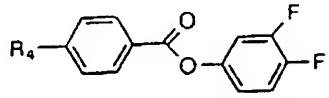

(6-2)

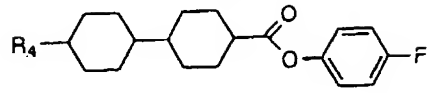

(6-3)

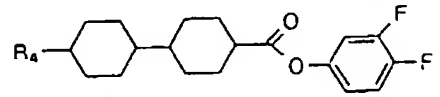

(7-1)

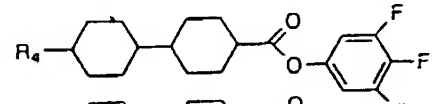

(7-2)

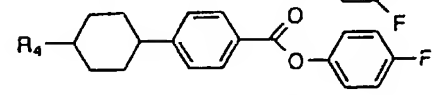

(7-3)

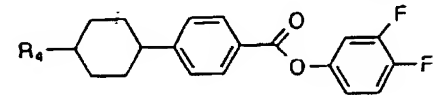

(7-4)

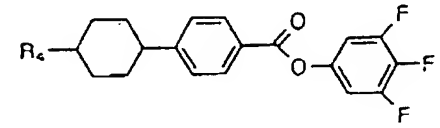

(7-5)

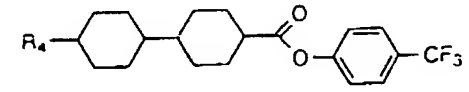

(7-6)

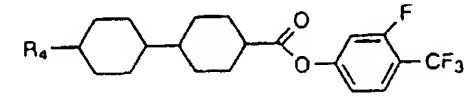

(7-7)

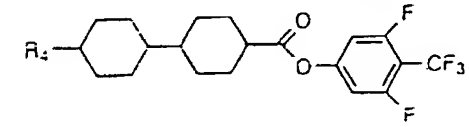

(7-8)

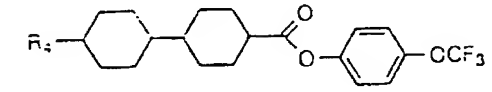

(7-9)

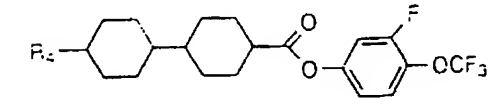

(7-10)

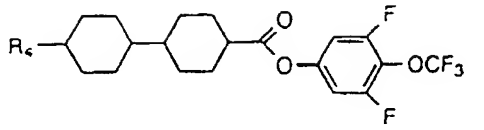

(7-11)

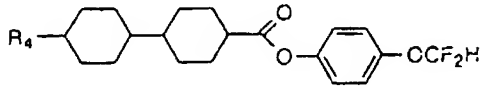

(7-12)

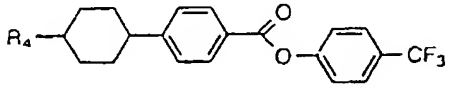

(7-13)

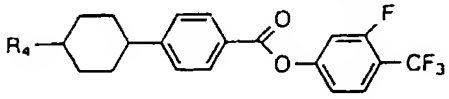

(7-14)

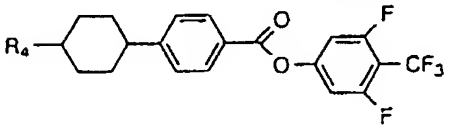

(7-15)

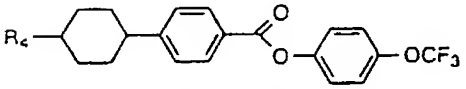

(7-16)

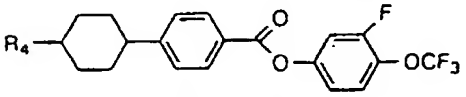

(7-17)

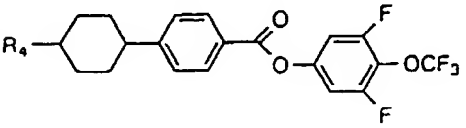

(7-18)

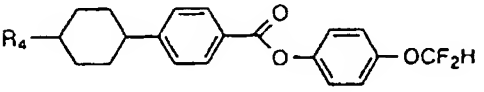

(7-19)

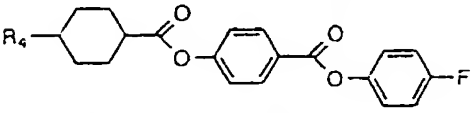

(7-20)

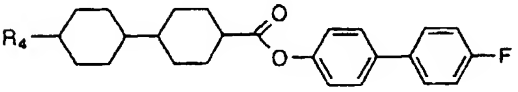

(7-21)

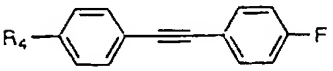

(7-22)

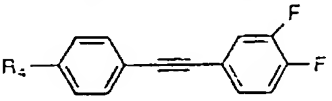

(7-23)


(7-24)


(7-25)


(7-26)

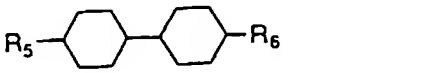

(7-27)

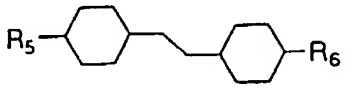

(7-28)

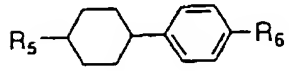
wherein, R_2, R_3 and R_4 denote the same meanings as the above-mentioned ones.

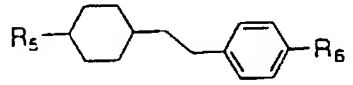
Compounds expressed by these general formulae (5) to (7) show positive dielectric anisotropies and they are particularly used with the intention of lowering a threshold voltage as components of compositions. Furthermore, they are used with the intentions of adjusting a viscosity, adjusting a refractive anisotropy value and enlarging a liquid crystal phase temperature range, as well as with the intention of improvement in sharpness.

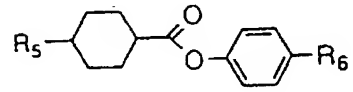
Also, among the above-mentioned second B components, there may be mentioned (8-1) to (8-8) and (9-1) to (9-13) as preferable examples of compounds of the general formulae (8) and (9), respectively.

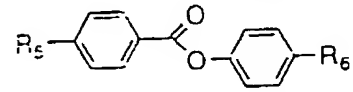

(8-1)

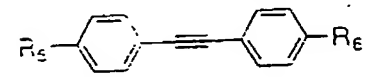

(8-2)

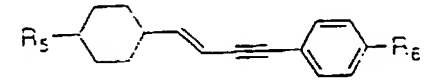

(8-3)

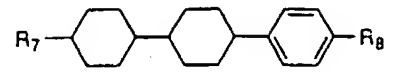

(8-4)

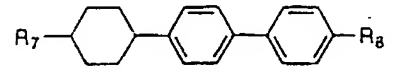

(8-5)

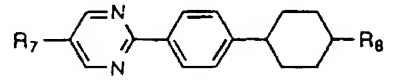

(8-6)

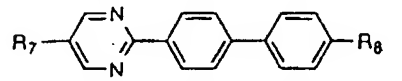

(8-7)

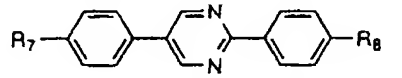

(8-8)

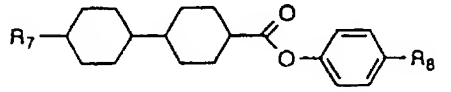

(9-1)

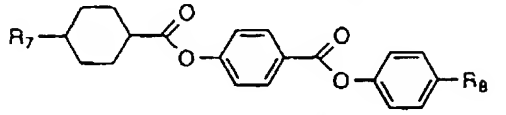

(9-2)

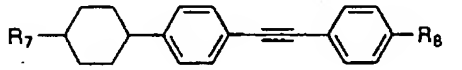

(9-3)

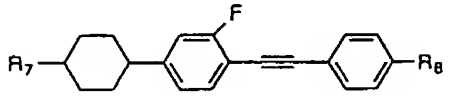

(9-4)

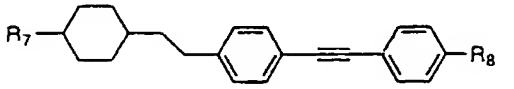

(9-5)

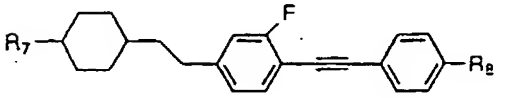

(9-6)

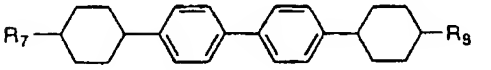

(9-7)

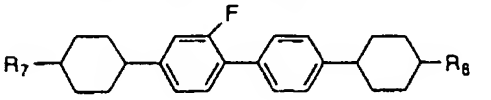

(9-8)


(9-9)


(9-10)


(9-11)


(9-12)


(9-13)

wherein, R_5 and R_6 denote the same meanings as the above-mentioned ones.

Compounds expressed by these general formulae (8) and (9) are compounds having negative or slightly positive dielectric anisotropies. Compounds of the general formula (8) are particularly used with the intentions of lowering a viscosity and/or adjusting a refractive anisotropy value. Furthemore, compounds of the general formula (9) are particularly used with the intentions of enlarging a nematic range such as increasing a clearing point and/or adjusting a refractive anisotropy value.

Compounds of the general formulae (5) to (9) are essential comopunds in the case of preparing liquid crystal compositions particularly for a STN display method and the conventional TN display method.

Amounts of compounds of the general formulae (5) to (9) used may be within a range of 1 to 99% by weight, preferably 10 to 97% by weight, and more preferably 40 to 95% by weight, in the case of preparing liquid crystal compositions particularly for a STN display method and the conventional TN display method. Furthermore, compounds of (2) to (4) may be used partly in such cases.

By using crystal liquid compositions according to the invention for TFT liquid crystal display devices, a sharpness and a viewing angle may be improved. Furthermore, since compounds of the formula (1) are low viscous compounds, a

response speed of liquid crystal display devices using them are improved very much.

Liquid crystal compositions according to the invention are prepared by conventional methods known per se. In general, there is used a method to dissolve various components each other at a higher temperature. However, liquid crystals may be dissolved in an organic solvent which can dissolve them, and mixed, and thereafter the solvent may be distilled off under a decreased pressure.

Furthermore, liquid crystal materials of the invention may be improved and optimized by means of suitable additives according to intended applications. Such additives are known by those skilled in the art and described in literatures etc.

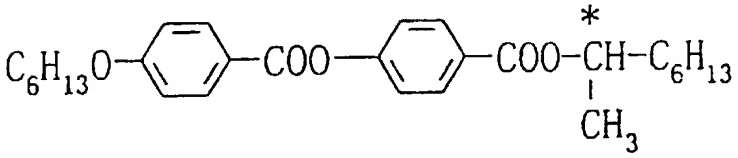
For example, dichromatic dyestuffs such as merocyanine type, styryl type, azoxy type, quinophthalone type, anthraquinone type and tetrazine type etc. may be added to use as liquid crystal compositions for a guest-host (GH) mode. Alternatively, they may be used as liquid crystal compositions for polymer disperse type liquid crystal display decices (PDLCD) represented by NCAP which is prepared by microcapsulating nematic liquid cystals and polymer network liquid crystal display devices (PNLCD) in which three-dimensional network macromolecules being made in liquid crystals. Furthermore, they may be used as liquid crystal compositions for an effective controlled birefringent (ECB) mode and a dinamic scattering (DS) mode.

Furthermore, there may be mentioned the following composition examples (Use Examples 1 to 36) as nematic liquid crystal

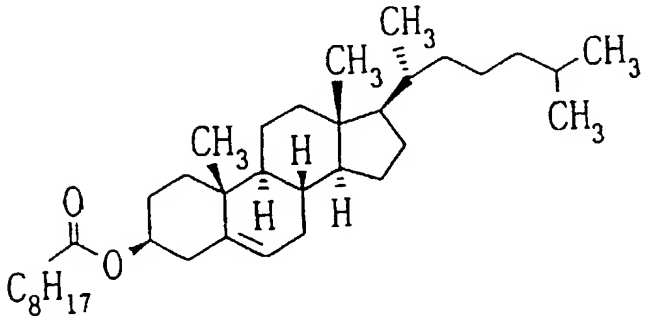
compositions containing compounds of the invention.

Compounds in composition examples are denoted by abbreviations according to definitions shown in Table 1. Furthermore, constitutions of optically active compounds are as follows.

CM-33



CN



In composition examples (use examples), "%" denotes "% by weight", and "part" denotes "part by weight" based on 100 parts by weight of a liquid crystal composition, unless otherwise described.

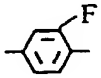
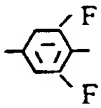
The determination temperature of viscosity (η) is 20.0 ℃, the detemination temperature and detemination wave length of refractive anisotropy (Δn) are 25.0 ℃ and 589nm respectively, the determination temperature of threshold voltage (Vth) is 25.0℃, and the determination temperature of pitch is 25.0℃.

Table 1

Expression modes of compounds using symbole

R —(A1)— Z1 ---------- Zn —(An)— X

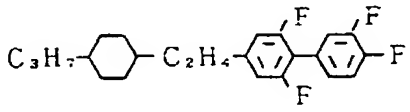
1) Left terminal R−	Symbol	3) Bonding group -Z1-, -Zn-	Symbol
C_nH_{2n+1}−	n−	$-C_2H_4-$	2
$C_nH_{2n+1}O$−	nO−	−COO−	E
$C_nH_{2n+1}OC_mH_{2m}$−	nOm−	−C≡C−	T
$CH_2=CH$−	V−		
$CH_2=CHC_nH_{2n}$−	Vn−		
$C_nH_{2n+1}CH=CH$−	nV−		
$C_nH_{2n+1}CH=CHC_mH_{2m}$−	nVm−		
$CF_2=CH$−	FFV−		
$CF_2=CHC_nH_{2n}$−	FFVn−		

2) Ring structuer -(A1)-, -(An)-	Symbol	4) Right terminal −X	Symbol
	B	−F	−F
		−Cl	−CL
		−CN	−C
	B (F)	$-OCF_3$	−OCF3
		$-OCF_2H$	−OCF2H
		$-C_nH_{2n+1}$	−n
	B (F, F)	$-OC_nH_{2n+1}$	−On
		$-C_mH_{2m}OC_nH_{2n+1}$	−mOn
		$-COOCH_3$	−EMe
	H	$-CH=CH_2$	−V
		$-C_nH_{2n}CH=CH_2$	−nV
	Py	$-CH=CHC_nH_{2n+1}$	−Vn
		$-C_mH_{2m}CH=CHC_nH_{2n+1}$	−mVn
	D	$-CH=CF_2$	−VFF
		$-C_nH_{2n}CH=CF_2$	−nVFF

5) Expression Examples

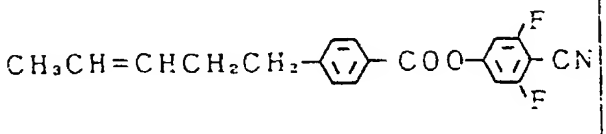
Example 1

3−H2B (F, F) B (F) −F



Example 2

1V2−BEB (F, F) −C



The following examples may be mentioned as nematic liquid crystal compositions containing compounds of the invention.

Use Example 1

V2-HH-VFF (No.25)	30.0%
V-BHH-VFF (No.7)	19.0%
V-BBH-VFF (No.9)	15.0%
3-HB-C	5.0%
1V2-BEB(F,F)-C	11.0%
3-HB-O2	4.0%
3-HB(F)TB-2	4.0%
3-H2BTB-2	4.0%
3-H2BTB-3	4.0%
3-H2BTB-4	4.0%

Use Example 2

V2-HH-VFF (No.25)	20.0%
1V-BHH-VFF (No.19)	10.0%
V-BBH-VFF (No.9)	6.0%
3-HB-C	10.0%
1V2-BEB(F,F)-C	12.0%
3-HB-O2	5.0%
3-HHB-1	10.0%
3-HHB-3	10.0%
3-HB(F)TB-2	5.0%
3-H2BTB-2	4.0%

3-H2BTB-3	4.0%
3-H2BTB-4	4.0%

Use Example 3

1V-BHH-VFF (No.19)	4.0%
1V2-BHH-VFF (No.118)	10.0%
V2-HB-C	10.0%
1V2-HB-C	10.0%
3-HB-C	26.0%
5-HB-C	12.0%
3-HB(F)-C	8.0%
2-BEB-C	3.0%
V2-HHB-1	8.0%
3-H2BTB-2	3.0%
3-H2BTB-3	3.0%
3-H2BTB-4	3.0%

Use Example 4

V2-HH-VFF (No.25)	9.0%
1V2-BEB(F,F)-C	11.0%
201-BEB(F)-C	5.0%
301-BEB(F)-C	9.0%
3-HB(F)-C	15.0%
101-HH-3	3.0%
4-BTB-O2	9.0%

2-HHB(F)-C	13.0%
3-HHB(F)-C	14.0%
3-H2BTB-2	4.0%
3-H2BTB-3	4.0%
3-H2BTB-4	4.0%

Use Example 5

1V2-BHH-VFF (No.118)	5.0%
V-BHH-2VFF (No.8)	10.0%
V2-HHH-VFF (No.29)	5.0%
2-BB-C	5.0%
2020-BB-C	4.0%
101-HB-C	10.0%
201-HB-C	7.0%
2-BEB-C	12.0%
5-PyB-F	8.0%
2-PyB-2	2.0%
3-PyB-2	2.0%
4-PyB-2	2.0%
V-HHB-1	5.0%
2-PyBH-3	5.0%
3-PyBH-3	5.0%
4-PyBH-3	5.0%
3-PyBB-F	3.0%
4-PyBB-F	3.0%
6-PyBB-2	2.0%

Use Example 6

V2-HH-VFF (No.25)	3.0%
3-PyB(F)-F	6.0%
3020-BEB-C	4.0%
3-BEB-C	12.0%
3-DB-C	10.0%
4-DB-C	10.0%
3-HEB-04	8.0%
4-HEB-02	6.0%
5-HEB-01	6.0%
3-HEB-02	5.0%
5-HEB-02	4.0%
3-HHB-1	6.0%
3-HHEBB-C	3.0%
3-HBEBB-C	3.0%
10-BEB-2	5.0%
4-HEB-3	3.0%
5-HEB-1	3.0%
6-PyB-02	3.0%

Use Example 7

V2-HH-VFF (No.25)	4.0%
1V-BHH-VFF (No.19)	3.0%
3-HB-C	20.0%
3-HHB-1	7.0%

3-HHB-3	8.0%
5-HEB-F	3.0%
7-HEB-F	3.0%
3-HHEB-F	1.0%
5-HHEB-F	1.0%
3-HEB-O4	4.0%
4-HEB-O2	3.0%
5-HEB-O1	3.0%
3-HEB-O2	2.5%
5-HEB-O2	2.0%
3-HB(F)TB-2	4.0%
3-HB(F)TB-3	4.0%
3-HB(F)VB-4	3.0%
3-H2BTB-2	3.0%
3-H2BTB-3	3.0%
3-H2BTB-4	3.0%
5-HHEBB-C	2.0%
3-HBEBB-C	3.0%
5-HBEBB-C	3.0%
3-HEBEB-F	3.0%
3-HH-EMe	2.5%
101-HBBH-3	2.0%

Use Example 8

V-BHH-2VFF (No.8)	6.0%
5-PyB(F)-F	13.0%

2-HB(F)-C	10.0%
3-HB(F)-C	12.0%
30-BB-C	8.0%
2-HHB-C	6.0%
3-HHB-C	6.0%
4-HHB-C	6.0%
2-HHB(F)-C	5.0%
3-HHB(F)-C	5.0%
3-PyBB-F	7.0%
4-PyBB-F	6.0%
5-HBB-C	5.0%
3-HB(F)EB(F)-C	5.0%

Use Example 9

V2-HH-VFF (No.25)	10.0%
2-BEB(F)-C	5.0%
3-BEB(F)-C	7.0%
4-BEB(F)-C	5.0%
5-BEB(F)-C	7.0%
103-HB(F)-C	6.0%
3-HHEB(F)-F	5.0%
4-HHEB(F)-F	5.0%
5-HHEB(F)-F	10.0%
2-HBEB(F)-C	5.0%
3-HBEB(F)-C	5.0%
4-HBEB(F)-C	5.0%

5-HBEB(F)-C	5.0%
3-HBTB-2	10.0%
V2-HH-3	5.0%
V2-HHB-1	5.0%

Use Example 10

V2-HH-VFF (No.25)	15.0%
1V2-BH-VFF (No.117)	5.0%
V2-HB-C	3.0%
4-BB-2	5.0%
3-BB-C	5.0%
5-BB-C	5.0%
2-HB(F)-C	5.0%
3-H2B-O2	5.0%
5-H2B-O3	10.0%
3-BEB-C	5.0%
5-HEB-O1	6.0%
5-HEB-O3	6.0%
5-BBB-C	3.0%
4-BPyB-C	3.0%
4-BPyB-5	3.0%
5-HB2B-4	4.0%
5-HBB2B-3	4.0%
V2-HH-101	3.0%
1V2-HBB-3	5.0%

Use Example 11

V2-HH-VFF (No.25)	5.0%
V-HH-VFF (No.1)	5.0%
5-H2B(F)-F	4.0%
7-HB(F)-F	10.0%
2-HHB(F)-F	12.0%
3-HHB(F)-F	12.0%
5-HHB(F)-F	12.0%
2-H2HB(F)-F	12.0%
3-H2HB(F)-F	6.0%
5-H2HB(F)-F	12.0%
2-HBB(F)-F	2.5%
3-HBB(F)-F	2.5%
5-HBB(F)-F	5.0%

Use Example 12

V2-HH-VFF (No.25)	7.0%
7-HB(F,F)-F	2.0%
2-HHB(F)-F	10.0%
3-HHB(F)-F	14.0%
5-HHB(F)-F	14.0%
2-H2HB(F)-F	4.0%
3-H2HB(F)-F	2.0%
5-H2HB(F)-F	4.0%
3-HHB(F,F)-F	8.0%

4-HHB(F,F)-F	4.0%
3-H2HB(F,F)-F	6.0%
4-H2HB(F,F)-F	5.0%
5-H2HB(F,F)-F	5.0%
3-HH2B(F,F)-F	8.0%
5-HH2B(F,F)-F	7.0%

Use Example 13

1V2-HHH-VFF (No.41)	8.0%
7-HB(F,F)-F	5.0%
3-HBB(F,F)-F	5.0%
5-HBB(F,F)-F	5.0%
3-HHB(F,F)-F	7.0%
5-HHB(F,F)-F	5.0%
3-HH2B(F,F)-F	8.0%
5-HH2B(F,F)-F	5.0%
3-H2HB(F,F)-F	10.0%
4-H2HB(F,F)-F	10.0%
5-H2HB(F,F)-F	10.0%
3-HHEB(F,F)-F	8.0%
4-HHEB(F,F)-F	3.0%
5-HHEB(F,F)-F	3.0%
3-HBEB(F,F)-F	2.0%
5-HBEB(F,F)-F	2.0%
3-HHHB(F,F)-F	2.0%
5-HH2BB(F,F)-F	2.0%

Use Example 14

1V2-BH-VFF (No.117)	5.0%
V2-BH-VFF (No.27)	5.0%
5-HB-F	2.0%
7-HB(F)-F	3.0%
2-HHB(F)-F	14.0%
3-HHB(F)-F	14.0%
5-HHB(F)-F	14.0%
3-HB-O2	5.0%
3-HHB-F	4.0%
3-HHB-1	6.0%
3-HHB-3	6.0%
2-HBB-F	6.0%
3-HBB-F	5.0%
3-HHEB-F	3.0%
5-HHEB-F	3.0%
3-HBEB-F	3.0%
3-HHEBB-F	2.0%

Use Example 15

V2-HH-VFF (No.25)	5.0%
1V2-BHH-VFF (No.118)	3.0%
7-HB(F,F)-F	7.0%
3-HB-CL	5.0%
7-HB-CL	5.0%

2-BTB-01	10.0%
2-HBB(F)-F	2.5%
3-HBB(F)-F	2.5%
5-HBB(F)-F	5.0%
3-HBB(F,F)-F	7.0%
5-HBB(F,F)-F	10.0%
2-HHB-CL	5.0%
3-HHB-CL	3.0%
3-HB(F)TB-2	6.0%
3-HB(F)TB-4	6.0%
2-H2BTB-2	4.0%
2-H2BTB-3	4.0%
3-H2HB(F)-CL	4.0%
5-H2HB(F)-CL	3.0%
3-H2BB(F,F)-F	3.0%

Use Example 16

V2-HH-VFF (No.25)	5.0%
1V2-BH-VFF (No.117)	5.0%
5-HB-F	10.0%
6-HB-F	5.0%
7-HB-F	5.0%
2-HHB-OCF3	5.0%
3-HHB-OCF3	5.0%
5-HHB-OCF3	5.0%
3-HH2B-OCF3	6.0%

5-HH2B-OCF3	6.0%
3-HB(F)B-3	4.0%
5-HB(F)B-3	4.0%
2-HBB(F)-F	10.0%
3-HBB(F)-F	10.0%
5-HBB(F)-F	15.0%

Use Example 17

V2-HH-VFF (No.25)	6.0%
V-HH-2VFF (No.116)	3.0%
1V2-HH-VFF (No.37)	3.0%
5-HB-F	3.0%
6-HB-F	3.0%
7-HB-F	3.0%
3-HHB-OCF2H	7.0%
5-HHB-OCF2H	7.0%
3-HHB(F,F)-OCF2H	9.0%
5-HHB(F,F)-OCF2H	9.0%
2-HHB-OCF3	6.0%
3-HHB-OCF3	6.0%
4-HHB-OCF3	6.0%
5-HHB-OCF3	6.0%
3-HH2B(F)-F	7.0%
5-HH2B(F)-F	7.0%
3-HHEB(F)-F	4.0%
5-HHEB(F)-F	5.0%

Use Example 18

V2-HH-VFF (No.25)	15.0%
3-HEB-04	23.4%
4-HEB-02	17.6%
5-HEB-01	17.6%
3-HEB-02	14.7%
5-HEB-02	11.7%

T_{NI}=67.7 (℃)

η =19.6 (mPa·s)

Use Example 19

V2-HHH-VFF (No.29)	15.0%
3-HEB-04	23.4%
4-HEB-02	17.6%
5-HEB-01	17.6%
3-HEB-02	14.7%
5-HEB-02	11.7%

T_{NI}=89.6 (℃)

η =25.7 (mPa·s)

Use Example 20

V2-HH-2VFF (No.115)	15.0%

3-HEB-04	23.4%
4-HEB-02	17.6%
5-HEB-01	17.6%
3-HEB-02	14.7%
5-HEB-02	11.7%

T_{NI}=69.5 (℃)

η =20.5 (mPa·s)

Use Example 21

V2-HH-VFF (No.25)	10.0%
V2-HH-2VFF (No.115)	8.0%
1V2-BEB(F,F)-C	5.0%
3-HB-C	25.0%
1-BTB-3	5.0%
3-HH-4	3.0%
3-HHB-1	11.0%
3-HHB-3	9.0%
3-H2BTB-2	4.0%
3-H2BTB-3	4.0%
3-H2BTB-4	4.0%
3-HB(F)TB-2	6.0%
3-HB(F)TB-3	6.0%

T_{NI}=93.3 (℃)

η =13.9 (mPa·s)

Δn=0.147

V_{th}=2.08 (V)

When 0.8 parts of CM33 was added to 100 parts of the above-mentioned composition, pitch was 10.5 μm.

Use Example 22

V2-HHH-VFF (No.29)	8.0%
201-BEB(F)-C	5.0%
301-BEB(F)-C	15.0%
401-BEB(F)-C	13.0%
501-BEB(F)-C	13.0%
2-HHB(F)-C	15.0%
3-HHB(F)-C	15.0%
3-HB(F)TB-2	4.0%
3-HB(F)TB-3	4.0%
3-HB(F)TB-4	4.0%
3-HHB-01	4.0%

T_{NI}=94.5 (℃)

η =85.5 (mPa·s)

Δn=0.149

V_{th}=0.90 (V)

Use Example 23

V2-HH-VFF (No. 25)	4.0%
V2-HH-2VFF (No. 115)	9.0%
V2-HHH-VFF (No. 29)	8.0%
5-PyB-F	4.0%
3-PyB(F)-F	4.0%
2-BB-C	5.0%
4-BB-C	4.0%
5-BB-C	5.0%
2-PyB-2	2.0%
6-PyB-O5	3.0%
3-PyBB-F	6.0%
4-PyBB-F	6.0%
5-PyBB-F	6.0%
3-HHB-1	6.0%
2-H2BTB-2	4.0%
2-H2BTB-3	4.0%
2-H2BTB-4	5.0%
3-H2BTB-2	5.0%
3-H2BTB-3	5.0%
3-H2BTB-4	5.0%

T_{NI}=99.4 (℃)

η=28.5 (mPa·s)

Δn=0.191

V_{th}=2.32 (V)

Use Example 24

V2-HH-VFF (No.25)	25.0%
3-DB-C	10.0%
4-DB-C	10.0%
2-BEB-C	12.0%
3-BEB-C	4.0%
3-PyB(F)-F	6.0%
5-HEB-O2	4.0%
5-HEB-5	5.0%
4-HEB-5	5.0%
1O-BEB-2	4.0%
3-HHB-1	6.0%
3-HHEBB-C	3.0%
3-HBEBB-C	3.0%
5-HBEBB-C	3.0%

T_{NI}=67.3 (℃)

η=31.0(mPa·s)

Δn=0.121

V_{th}=1.28(V)

Use Example 25

V2-HH-2VFF (No.115)	4.0%
3-HB-C	18.0%
7-HB-C	3.0%

101-HB-C	10.0%
3-HB(F)-C	10.0%
4-PyB-2	2.0%
101-HH-3	7.0%
2-BTB-01	7.0%
3-HHB-1	7.0%
3-HHB-F	4.0%
3-HHB-01	4.0%
3-HHB-3	8.0%
3-H2BTB-2	3.0%
3-H2BTB-3	3.0%
2-PyBH-3	4.0%
3-PyBH-3	3.0%
3-PyBB-2	3.0%

T_{NI}=81.4 (℃)

η=16.9(mPa·s)

Δn=0.137

V_{th}=1.77(V)

Use Example 26

1V2-HH-VFF (No.37)	5.0%
1V2-HH-2VFF (No.38)	8.0%
201-BEB(F)-C	5.0%
301-BEB(F)-C	12.0%
501-BEB(F)-C	4.0%

1V2-BEB(F,F)-C	10.0%
3-HH-EMe	5.0%
3-HB-O2	10.0%
7-HEB-F	2.0%
3-HHEB-F	2.0%
5-HHEB-F	2.0%
3-HBEB-F	4.0%
201-HBEB(F)-C	2.0%
3-HB(F)EB-C	2.0%
3-HBEB(F,F)-C	2.0%
3-HHB-F	4.0%
3-HHB-O1	4.0%
3-HHB-3	13.0%
3-HEBEB-F	2.0%
3-HEBEB-1	2.0%

Use Example 27

1V-HH-VFF (No.13)	5.0%
1V-HH-2VFF (No.14)	5.0%
V2-HHH-VFF (No.29)	8.0%
201-BEB(F)-C	5.0%
301-BEB(F)-C	12.0%
501-BEB(F)-C	4.0%
1V2-BEB(F,F)-C	16.0%
3-HH-4	3.0%
3-HHB-F	3.0%

3-HHB-O1	4.0%
3-HBEB-F	4.0%
3-HHEB-F	7.0%
5-HHEB-F	7.0%
3-H2BTB-2	4.0%
3-H2BTB-3	4.0%
3-H2BTB-4	4.0%
3-HB(F)TB-2	5.0%

Use Example 28

V2-HH-VFF (No.25)	20.0%
V2-HHH-VFF (No.29)	4.0%
2-BEB-C	12.0%
3-BEB-C	4.0%
4-BEB-C	6.0%
3-HB-C	28.0%
5-HEB-O1	8.0%
3-HEB-O2	6.0%
5-HEB-O2	5.0%
3-HHB-1	7.0%

T_{NI}=60.4 (℃)

η =18.2(mPa·s)

Δn=0.112

V_{th}=1.31(V)

Use Example 29

1V2-HH-VFF (No.37)	5.0%
1V-HH-VFF (No.13)	5.0%
1V2-HH-2VFF (No.38)	5.0%
1V-HH-2VFF (No.14)	5.0%
2-BEB-C	10.0%
5-BB-C	12.0%
7-BB-C	7.0%
1-BTB-3	7.0%
10-BEB-5	12.0%
2-HHB-1	4.0%
3-HHB-F	4.0%
3-HHB-1	7.0%
3-HHB-O1	4.0%
3-HHB-3	13.0%

Use Example 30

V2-HH-2VFF (No.115)	20.0%
1V2-BEB(F,F)-C	6.0%
3-HB-C	18.0%
2-BTB-1	10.0%
5-HH-VFF	10.0%
1-BHH-VFF	8.0%
1-BHH-2VFF	11.0%
3-H2BTB-2	5.0%

3-H2BTB-3	4.0%
3-H2BTB-4	4.0%
3-HHB-1	4.0%

T_{NI}=83.1 (℃)

η=11.7(mPa·s)

Δn=0.132

V_{th}=2.10(V)

Use Example 31

V2-HHH-VFF (No.29)	8.0%
2-HB-C	5.0%
3-HB-C	12.0%
3-HB-O2	15.0%
2-BTB-1	3.0%
3-HHB-F	4.0%
3-HHB-O1	5.0%
3-HHB-3	14.0%
3-HHEB-F	4.0%
5-HHEB-F	4.0%
2-HHB(F)-F	7.0%
3-HHB(F)-F	7.0%
5-HHB(F)-F	7.0%
3-HHB(F,F)-F	5.0%

T_{NI}=103.0(℃)

η=17.2(mPa·s)

Δn=0.099

V_{th}=2.56(V)

Use Example 32

V2-HH-VFF (No.25)	3.0%
V2-HHH-VFF (No.29)	5.0%
3-BEB(F)-C	8.0%
3-HB-C	8.0%
V-HB-C	8.0%
1V-HB-C	8.0%
3-HH-2V	14.0%
3-HH-2V1	7.0%
V2-HHB-1	15.0%
3-HHEB-F	7.0%
3-H2BTB-2	6.0%
3-H2BTB-3	6.0%
3-H2BTB-4	5.0%

T_{NI}=101.3(℃)

η=15.2(mPa·s)

Δn=0.132

V_{th}=2.25(V)

Use Example 33

V2-HH-2VFF (No.115)	31.0%
1V2-BEB(F,F)-C	12.0%
3-HB-C	4.0%
3-HB-O2	5.5%
3-HHB-1	3.5%
1-BHH-VFF	20.0%
3-HB(F)TB-2	4.0%
3-HB(F)TB-3	4.0%
3-HB(F)TB-4	4.0%
3-H2BTB-2	4.0%
3-H2BTB-3	4.0%
3-H2BTB-4	4.0%

T_{NI}=100.4(℃)

η=14.1(mPa·s)

Δn=0.133

V_{th}=2.16(V)

When 2.0 parts of CN was added to 100 parts of the above-mentioned composition, pitch was 10.6 μm.

Use Example 34

V2-HH-VFF (No.25)	28.0%
1V2-BEB(F,F)-C	12.0%
3-HB-C	4.0%

3-HB-02	5.5%
3-HHB-1	8.5%
1-BHH-VFF	20.0%
3-HB(F)TB-2	5.0%
3-HB(F)TB-3	5.0%
3-H2BTB-2	4.0%
3-H2BTB-3	4.0%
3-H2BTB-4	4.0%

T_{NI}=100.5(℃)

η=13.9(mPa·s)

Δn=0.132

V_{th}=2.14(V)

When 1.81 parts of CN was added to 100 parts of the above-mentioned composition, pitch was 12.3 μm.

Use Example 35

V2-HH-VFF (No.25)	15.0%
201-BEB(F)-F	10.0%
301-BEB(F)-F	26.0%
1V2-BEB(F,F)-C	5.0%
2-HHB(F)-C	14.0%
3-HHB(F)-C	14.0%
3-HB(F)TB-2	5.0%
3-HB(F)TB-3	5.0%
3-HHB-1	6.0%

T_{NI}=85.3 (℃)

η=51.1 (mPa·s)

Δn=0.143

V_{th}=0.96 (V)

Use Example 36

V2-HH-VFF (No.25)	8.0%
2-HBEB(F,F)-F	3.0%
3-HBEB(F,F)-F	5.0%
5-HBEB(F,F)-F	3.0%
3-HB-C	20.0%
1V2-BEB(F,F)-C	30.0%
3-HHB-3	10.0%
3-HHB-01	5.0%
3-HHEB-F	3.0%
5-HHEB-F	3.0%
3-H2BTB-2	5.0%
3-H2BTB-3	5.0%

T_{NI}=77.0 (℃)

η=34.0 (mPa·s)

Δn=0.137

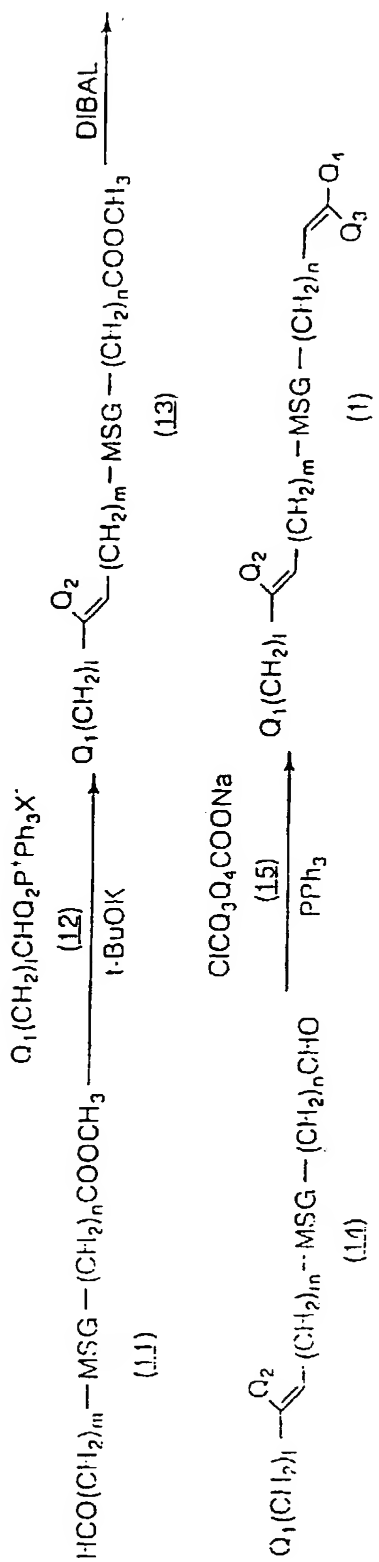
V_{th}=0.98 (V)

Preparation of compounds

Compounds (1) of the present invention can be prepared easily

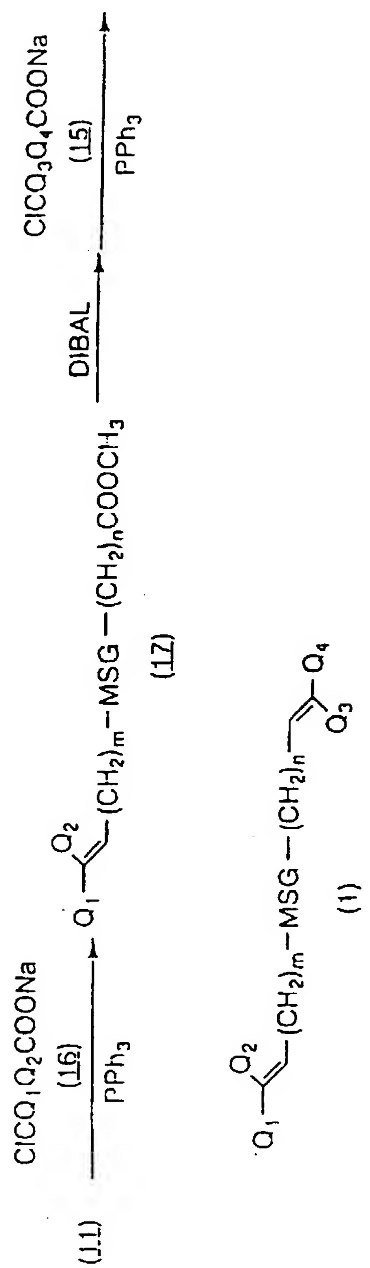
by utilizing conventional organic synthetic chemical methods. They can be synthesized easily by selecting and combining appropriately known reactions described for example in books such as Organic Synthesis, Organic Reactions, Shin Zikken Kagaku Koza, and magazines.

That is, a liquid crystalline compound of the present invention can be prepared by reacting a triphenyl phosphonium halide derivative (12) with an aldehyde derivative (11) in an ether solvent such as THF and diethyl ether etc. in the presence of a base such as sodium methylate, potassium-t-butoxide (t-BuOK) and butyl lithium etc. to obtain (13) according to the known method which utilizes Wittig reaction such as method described in Organic Reactions, Vol.14, Chapter 3 etc., reacting diisobutyl aluminium halide (hereinafter abbreviated as DIBAL) with (13) in toluene to obtain an aldehyde derivative (14), and then reacting (15) and triphenylphosphine with (14) to prepare the compound (1) of the present invention.



X= Cl, Br, I   MSG= $(A_1\text{-}Z_1)_p-(A_2\text{-}Z_2)_q-A_3\text{-}Z_3\text{-}A_4$

Furthermore, in the case of $Q_1=Q_2\neq H$ and l=0, the following method is preferable. That is, compound (1) of the present invention can be prepared by reacting an aldehyde derivative (11) with (16) and triphenylphosphine in N,N-dimethyl formamide (hereinafter abbreviated as DMF) to obtain (17), and treating it by the same series of the above-mentioned operations for obtaining (1) from (13).



$Q_1 = Q_2 \neq H$, $l = 0$, $X = Cl, Br, I$ $MSG = (A_1\text{-}Z_1)_p-(A_2\text{-}Z_2)_q-A_3\text{-}Z_3\text{-}A_4$

Furthermore, compounds in which A_1, A_2, A_3 and A_4 being silacyclohexane ring can be prepared according to methods disclosed in Toku-Kai-Hei 7-70148, Toku-Kai-Hei 7-112990 and Toku-Kai-Hei 7-149770.

Liquid crystalline compounds of the invention thus obtained show wide liquid crystal phase temperature ranges, are low viscous, have high elastic constant ratios K_{33}/K_{11}, are mixed easily with other various liquid crystal materials even at lower temperatures, and also are quite superior as constitution components of nematic liquid crystal compositions suitable for a STN type display method.

Examples

The invention is explained in more detail by the following examples, but the invention is not restricted by these examples. Herein, constitutions of compounds were confirmed by nuclear magnetic resonance spectrum (hereinafter abbreviated as 1H-NMR) and mass spectrum (hereinafter abbreviated as MS) etc. In examples, d denotes doublet, t denotes triplet, m denotes multiplet, and J denotes a coupling constant in NMR. M^+ denotes a molecular ion peak and values in parentheses denote an ion strength in MS. Cr denotes a cryatal phase, S denotes a smetic phase, N denotes a nematic phase, Iso denotes an isotropic liquid phase and phase transfer temperature units are all ℃.

Example 1

Preparation of 1-(2,2-difluoroethenyl)-trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexane (compound (No. 25) of the formula (1) in which A_3 and A_4 are trans-1,4-cyclohexylene groups; Z_3 is

a covalent bond; Q_1 and Q_2 are H; Q_3 and Q_4 are F; l, n, p and q are 0; and m is 2)

the first step

A mixture of 165.6g (463.6 mmol) of methyl triphenyl phosphonium bromide and 1.5 liters of THF was cooled to -50 ℃ under a gas stream of nitrogen. To the mixture, 57.2g (509.8 mmol) of t-BuOK was added and stirred for 1 hour. To the mixture, a solution of 100.0g (356.6 mmol) of methyl trans-4-(trans-4-(2-formylethyl)cyclohexyl)cyclohexane carboxylate in 1 liter of THF was added dropwise with maintaining the temperature below -50 ℃. After dropwise addition, the reaction temperature was increased gradually to the room temperature, and stirring was carried out further for 5 hours. The solvent was distilled off under a decreased pressure, then 500 ml of water was added and the mixture was extracted with 500 ml of toluene. The organic layer was washed with 200 ml of water for three times and dried with anhydrous magnesium sulphate.

The solvent was distilled off under a decreased pressure, and the residue was subjected to silica gel column chromatography (eluent: a mixed solvent of ethyl acetate/heptane = 1/10), to obtain 34.8g of crude methyl trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexane carboxylate.

the second step

34.8g (125.0 mmol) of the crude product was dissolved in 500 ml of toluene, to which 125 ml of 1.0M solution of DIBAL in toluene was added dropwise under a gas stream of nitrogen with maintaining the temperature below -50 ℃. After stirring at the

same temperature for 1 hour, the reaction was ended by pouring the reaction solution gradually into water. It was washed with 300 ml of water for three times and dried with anhydrous magnesium sulphate. The solvent was distilled off under a decreased pressure, to obtain 30.3g of crude trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexane carbaldehyde.

the third step

30.3g (122.0 mmol) of crude trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexane carbaldehyde and 41.6g (158.6 mmol) of triphenylphosphine were added to 600 ml of a mixed solvent of toluene/DMF (1/5) with stirring under a gas flow of nitrogen, the temperature of which being increased. Once the temperature becoming 100~110℃, a solution of 37.2g (244.0 mmol) of sodium chlorodifluoroacetate in 400 ml of DMF was added dropwise with maintaining the same temperature. After completion of dropwise addition, it was stirred for 30 minutes and allowed to cool to the room temperature. 1 liter of water and 1 liter of heptane were added to the reaction mixture, stirred thoroughly, and thereafter filtered with Celite. Then, the water layer was extracted with 500 ml of heptane, the organic layer was washed with 700 ml of water for three times and dried with anhydrous magnesium sulphate.

The solvent was distilled off under a decreased pressure and the residue was subjected to silica gel column chromatograpy (eluent: heptane), to obtain 13.3g of crude 1-(2,2-difluoroethenyl)-trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexane. The crude product was recrystallized from Solmix,

to obtain 13.3g of the title compound (yield 13.2%).

Phase transfer temperature: Cr -7.1 S -4.9 N 49.7 Iso

^{1}H-NMR: δ:(ppm): 0.50~2.38 (m, 24H), 3.99 (d, d, d, 1H, J_{H-F}=22.9, 9.2, J=6.3), 4.80~5.15 (m, 2H), 5.82 (d, d, t, 1H, J_{H-F}=17.2, 10.0, J=6.7), MS:m/e=282(M^+), 225, 211, 135, 95, 81, 67.

Example 2

Preparation of 1-(4,4-difluoro-3-butenyl)-trans-4-(trans-4-(trans-4-ethenylcyclohexyl)cyclohexyl)cyclohexane (compound (No. 6) of the formula (1) in which A_2, A_3 and A_4 are trans-1,4-cyclohexylene groups; Z_2 and Z_3 are covalent bonds; Q_1 and Q_2 are H; Q_3 and Q_4 are F; l, m and p are 0; q is 1; and n is 2)

the first step

A mixture of 128.1g (358.6 mmol) of methyl triphenyl phosphonium bromide and 1.5 liters of THF was cooled to -50 ℃ under a gas stream of nitrogen. To the mixture, 44.3g (394.8 mmol) of t-BuOK was added and stirred for 1 hour. To the mixture, a solution of 100.0g (275.8 mmol) of methyl 2-(trans-4-(trans-4-(trans-4-formylcyclohexyl)cyclohexyl)cyclohexyl)ethane-carboxylate in 1 liter of THF was added dropwise with maintaining the temperature below -50 ℃. After dropwise addition, the reaction temperature was increased gradually to the room temperature, and stirring was carried out further for 5 hours. The solvent was distilled off under a decresed pressure, 500 ml of water was added and the mixture was extracted with 500 ml of toluene. The organic layer was washed with 200 ml of water for three times and dried with anhydrous magnesium sulphate.

The solvent was distilled off under a decreased pressure, and the residue was subjected to silica gel column chromatography (eluent: a mixed solvent of ethyl acetate/heptane = 1/8), to obtain 37.8g of crude methyl 2-(trans-4-(trans-4-(trans-4-ethenylcyclohexyl)cyclohexyl)cyclohexyl)ethane carboxylate.

the second step

37.8g (104.8 mmol) of the crude product was dissolved in 500 ml of toluene, to which 105 ml of 1.0M solution of DIBAL in toluene was added dropwise under a gas stream of nitrogen with maintaining the temperature below -50 ℃. After stirring at the same temperature for 1 hour, the reaction was ended by pouring the reaction solution gradually into water. It was washed with 300 ml of water for three times and dried with anhydrous magnesium sulphate. The solvent was distilled off under a decreased pressure, to obtain 32.9g of crude 3-(trans-4-(trans-4-(trans-4-ethenylcyclohexyl)cyclohexyl)cyclohexyl)propanal.

the third step

32.9g (99.5 mmol) of crude 3-(trans-4-(trans-4-(trans-4-ethenylcyclohexyl)cyclohexyl)cyclohexyl)propanal and 33.9g (129.2 mmol) of triphenylphosphine were added to 600 ml of a mixed solvent of toluene/DMF (1/5) with stirring under a gas flow of nitrogen, the temperature of which being increased. Once the temperature becoming 100~110℃, a solution of 30.3g (198.7 mmol) of sodium chlorodifluoroacetate in 300 ml of DMF was added dropwise with maintaining the same temperature. After completion of dropwise addition, it was stirred for 30 minutes and allowed to cool to the room temperature. 1 liter of water and 1 liter of

heptane were added to the reaction mixture, stirred thoroughly, and thereafter filtered with Celite. Then, the water layer was extracted with 500 ml of heptane, the organic layer was washed with 700 ml of water for three times and dried with anhydrous magnesium sulphate.

The solvent was distilled off under a decreased pressure and the residue was subjected to silica gel column chromatograpy (eluent: heptane), to obtain crude 1-(4,4-difluoro-3-butenyl)-trans-4-(trans-4-(trans-4-ethenylcyclohexyl)cyclohexyl) cyclohexane. The crude product was recrystallized from Solmix, to obtain 14.5g of the title compound (yield 14.4%).

MS:m/e=364(M^+).

Example 3

Preparation of 1-(2,2-difluoroethenyl)-trans-4-(trans-4-(4-(3-butenyl)phenyl)cyclohexyl)cyclohexane (compound (No. 31) of the formula (1) in which A_2 is 1,4-phenylene group; rings A_3 and A_4 are trans-1,4-cyclohexylene groups; Z_2 and Z_3 are covalent bonds; Q_1 and Q_2 are H; Q_3 and Q_4 are F; l, n and p are 0; q is 1; and m is 2)

the first step

A mixture of 130.3g (364.8 mmol) of methyl triphenyl phosphonium bromide and 1.5 liters of THF was cooled to -50 ℃ under a gas stream of nitrogen. To the mixture, 45.0g (401.0 mmol) of t-BuOK was added and stirred for 1 hour. To the mixture, a solution of 100.0g (280.5 mmol) of methyl trans-4-(trans-4-(4-(2-formylethyl)phenyl)cyclohexyl)cyclohexane carboxylate in 1 liter of THF was added dropwise with

maintaining the temperature below -50 ℃. After dropwise addition, the reaction temperature was increased gradually to the room temperature, and stirring was carried out further for 5 hours.

The solvent was distilled off under a decreased pressure, then 500 ml of water was added and the mixture was extracted with 500 ml of toluene. The organic layer was washed with 200 ml of water for three times and dried with anhydrous magnesium sulphate. The solvent was distilled off under a decreased pressure, and the residue was subjected to silica gel column chromatography (eluent: a mixed solvent of ethyl acetate/heptane = 1/8), to obtain 37.8g of crude methyl trans-4-(trans-4-(4-(3-butenyl)phenyl)cyclohexyl)cyclohexane carboxylate.

the second step

37.8g (106.6 mmol) of the crude product was dissolved in 500 ml of toluene, to which 107 ml of 1.0M solution of DIBAL in toluene was added dropwise under a gas stream of nitrogen with maintaining the temperature below -50 ℃. After stirring at the same temperature for 1 hour, the reaction was ended by pouring the reaction solution gradually into water. It was washed with 300 ml of water for three times and dried with anhydrous magnesium sulphate. The solvent was distilled off under a decreased pressure, to obtain 31.8g of crude trans-4-(trans-4-(4-(3-butenyl)phenyl)cyclohexyl)cyclohexane carbaldehyde.

the third step

31.8g (98.0 mmol) of crude trans-4-(trans-4-(4-(3-butenyl)phenyl)cyclohexyl)cyclohexane carbaldehyde and 33.4g

(127.3 mmol) of triphenylphosphine were added to 600 ml of a mixed solvent of toluene/DMF (1/5) with stirring under a gas flow of nitrogen, the temperature of which being increased. Once the temperature becoming 100~110℃, a solution of 29.9g (196.1 mmol) of sodium chlorodifluoroacetate in 300 ml of DMF was added dropwise with maintaining the same temperature. After completion of dropwise addition, it was stirred for 30 minutes and allowed to cool to the room temperature. 1 liter of water and 1 liter of heptane were added to the reaction mixture, stirred thoroughly, and thereafter filtered with Celite. Then, the water layer was extracted with 500 ml of heptane, the organic layer was washed with 700 ml of water for three times and dried with anhydrous magnesium sulphate.

The solvent was distilled off under a decreased pressure and the residue was subjected to silica gel column chromatograpy (eluent: heptane), to obtain crude 1-(2,2-difluoroethenyl)-trans-4-(trans-4-(4-(3-butenyl)phenyl)cyclohexyl)cyclohexane. The crude product was recrystallized from Solmix, to obtain 14.4g of the title compound (yield 14.3%).

MS:m/e=358(M^+).

Example 4

Preparation of 1-(2,2-difluoroethenyl)-trans-4-(4-(4-trans-4-(3-butenyl)cyclohexyl)phenyl)phenyl)cyclohexane (compound (No. 35) of the formula (1) in which A_1 and A_4 are trans-1,4-cyclohexylene groups; A_2 and A_3 are 1,4-phenylene groups; Z_1, Z_2 and Z_3 are covalent bonds; Q_1 and Q_2 are H; Q_3 and Q_4 are F; l and n are 0; p and q are 1; and m is 2)

the first step

A mixture of 107.4g (300.6 mmol) of methyl triphenyl phosphonium bromide and 1 liter of THF was cooled to -50℃ under a gas stream of nitrogen. To the mixture, 37.1g (330.6 mmol) of t-BuOK was added and stirred for 1 hour. To the mixture, a solution of 100.0g (231.2 mmol) of methyl trans-4-(4-(4-(trans-(2-formylethyl)cyclohexyl)phenyl)phenyl)cyclohexane carboxylate in 1 liter of THF was added dropwise with maintaining the temperature below -50 ℃. After dropwise addition, the reaction temperature was increased gradually to the room temperature, and stirring was carried out further for 5 hours. The solvent was distilled off under a decresed pressure, 500 ml of water was added and the mixture was extracted with 500 ml of toluene. The organic layer was washed with 200 ml of water for three times and dried with anhydrous magnesium sulphate.

The solvent was distilled off under a decreased pressure, and the residue was subjected to silica gel column chromatography (eluent: a mixed solvent of ethyl acetate/heptane = 1/7), to obtain 33.9g of crude methyl trans-4-(4-(4-(trans-4-(3-butenyl)cyclohexyl)phenyl)phenyl)cyclohexane carboxylate.

the second step

33.9g (78.7 mmol) of the crude product was dissolved in 350 ml of toluene, to which 79 ml of 1.0M solution of DIBAL in toluene was added dropwise under a gas stream of nitrogen with maintaining the temperature below -50 ℃. After stirring at the same temperature for 1 hour, the reaction was ended by pouring the reaction solution gradually into water. It was washed with

200 ml of water for three times and dried with anhydrous magnesium sulphate. The solvent was distilled off under a decreased pressure, to obtain 28.4g of crude trans-4-(4-(4-(trans-4-(3-butenyl)cyclohexyl)phenyl)phenyl)cyclohexane carbaldehyde.

the third step

28.4g (70.9 mmol) of crude trans-4-(4-(4-(trans-4-(3-butenyl)cyclohexyl)phenyl)phenyl)cyclohexane carbaldehyde and 24.2g (92.3 mmol) of triphenylphosphine were added to 400 ml of a mixed solvent of toluene/DMF (1/5) with stirring under a gas flow of nitrogen, the temperature of which being increased. Once the temperature becoming 100~110℃, a solution of 21.6g (141.7 mmol) of sodium chlorodifluoroacetate in 200 ml of DMF was added dropwise with maintaining the same temperature. After completion of dropwise addition, it was stirred for 30 minutes and allowed to cool to the room temperature. 600 ml of water and 600 ml of heptane were added to the reaction mixture, stirred thoroughly, and thereafter filtered with Celite. Then, the water layer was extracted with 300 ml of heptane, the organic layer was washed with 350 ml of water for three times and dried with anhydrous magnesium sulphate.

The solvent was distilled off under a decreased pressure and the residue was subjected to silica gel column chromatograpy (eluent: heptane), to obtain crude 1-(2,2-difluoroethenyl)-trans-4-(4-(4-(trans-4-(3-butenyl)cyclohexyl)phenyl)phenyl)cyclohexane. The crude product was recrystallized from Solmix, to obtain 13.9g of the title compound (yield 13.8%).

MS:m/e=434(M^+).

Example 5

Preparation of 1-(4,4-difluoro-3-butenyl)-trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexane (compound (No. 115) of the formula (1) in which A_3 and A_4 are trans-1,4-cyclohexylene groups; Z_3 is a covalent bond; Q_1 and Q_2 are H; Q_3 and Q_4 are F; l, p and q are 0; and m and n are 2)

the first step

A mixture of 66.4g (193.7 mmol) of methoxymethyltriphenyl phosphonium chloride and 600 ml of THF was cooled to -50℃ under a gas stream of nitrogen. To the mixture, 20.1g (179.1 mmol) of t-BuOK was added and stirred for 1 hour. To the mixture, a solution of 37.0g (148.9 mmol) of trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexane carbaldehyde in 400 ml of THF was added dropwise with maintaining the temperature below -50 ℃. After dropwise addition, the reaction temperature was increased gradually to the room temperature, and stirring was carried out further for 5 hours. The solvent was distilled off under a decresed pressure, 250 ml of water was added and the mixture was extracted with 300 ml of toluene. The organic layer was washed with 200 ml of water for three times and dried with anhydrous magnesium sulphate. The solvent was distilled off under a decreased pressure, and the residue was subjected to silica gel column chromatography (eluent: a mixed solvent of toluene/heptane= 3/7), to obtain 16.1g of crude 1-(2-methoxyethenyl)-trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexane.

the second step

16.0g (57.9 mmol) of the crude product was dissolved in 200 ml of toluene, 30.6g (578.3 mmol) of 87% formic acid was added and heating to reflux was carried out for 3 hours. The reaction solution was washed in order with 200 ml of water twice, 100 ml of a saturated sodium hydrogen carbonate solution for three times and 200 ml of water for three times, and then dried with anhydrous magnesium sulphate. The solvent was distilled off under a decreased pressure, to obtain 14.8g of crude trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexyl acetaldehyde.

the third step

A mixture of 25.2g (73.5 mmol) of methoxymethyltriphenyl phosphonium chloride and 300 ml of THF was cooled to -50℃ under a gas stream of nitrogen. To the mixture, 7.6g (67.8 mmol) of t-BuOK was added and stirred for 1 hour. To the mixture, a solution of 14.8g (56.5 mmol) of trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexyl acetaldehyde in 150 ml of THF was added dropwise with maintaining the temperature below -50 ℃. After dropwise addition, the reaction temperature was increased gradually to the room temperature, and stirring was carried out further for 5 hours. The solvent was distilled off under a decresed pressure, 150 ml of water was added and the mixture was extracted with 200 ml of toluene. The organic layer was washed with 100 ml of water for three times and dried with anhydrous magnesium sulphate. The solvent was distilled off under a decreased pressure, and the residue was subjected to silica gel column chromatography (eluent: a mixed solvent of toluene/heptane= 3/7), to obtain 12.8g of crude 1-(3-methoxypropenyl)-

trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexane.

the fourth step

12.1g (41.7 mmol) of the crude product was dissolved in 200 ml of toluene, 22.0g (415.8 mmol) of 87% formic acid was added and heating to reflux was carried out for 3 hours. The reaction solution was washed in order with 200 ml of water twice, 100 ml of a saturated sodium hydrogen carbonate solution for three times and 200 ml of water for three times, and then dried with anhydrous magnesium sulphate. The solvent was distilled off under a decreased pressure, to obtain 11.5g of crude trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexyl propanal.

the fifth step

11.5g (41.6 mmol) of crude trans-4-(trans-4-(3-butenyl)cyclohexyl)cyclohexyl propanal and 14.2g (54.1 mmol) of triphenylphosphine were added to 100 ml of a mixed solvent of toluene/DMF (1/5) with stirring under a gas flow of nitrogen, the temperature of which being increased. Once the temperature becoming 100~110℃, a solution of 12.7g (83.3 mmol) of sodium chlorodifluoroacetate in 100 ml of DMF was added dropwise with maintaining the same temperature. After completion of dropwise addition, it was stirred for 30 minutes and allowed to cool to the room temperature. 200 ml of water and 200 ml of heptane were added to the reaction mixture, stirred thoroughly, and thereafter filtered with Celite. Then, the water layer was extracted with 200 ml of heptane, the organic layer was washed with 300 ml of water for three times and dried with anhydrous magnesium sulphate. The solvent was distilled off under a

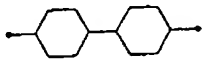
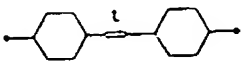
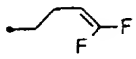
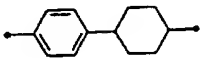
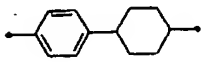
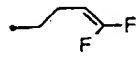
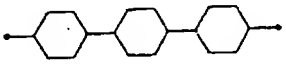
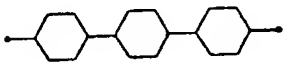
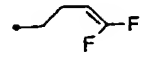
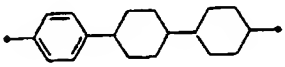
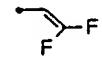
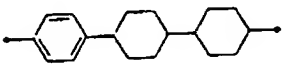
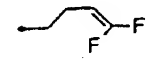
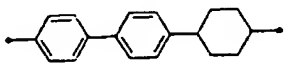
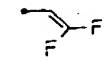
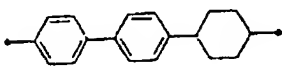
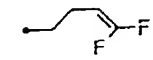
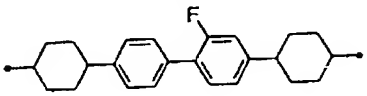
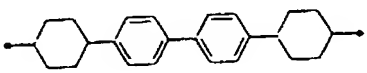
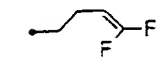
decreased pressure and the residue was subjected to silica gel column chromatograpy (eluent: heptane), to obtain crude 1-(4,4-difluoro-3-butenyl)-trans-4-(trans-4-(3-butenyl)cyclohexyl) cyclohexane. The crude product was recrystallized from Solmix, to obtain 5.1g of the title compound (yield 11.7%).

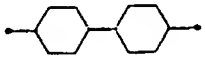
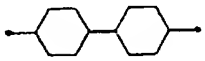
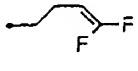
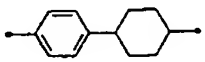
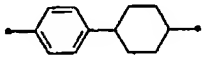
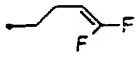
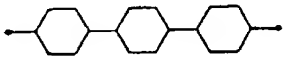
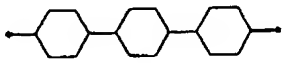
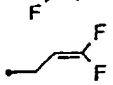
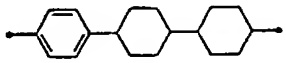
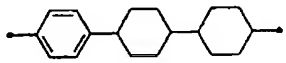
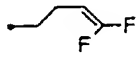
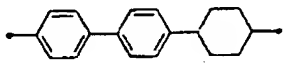
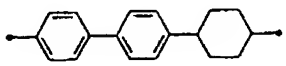
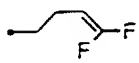
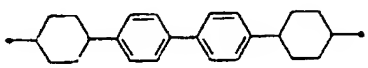
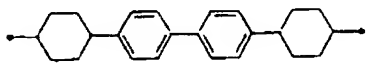
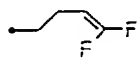
Phase transfer temperature: Cr -7.0 SB 49.0 N 69.0 Iso

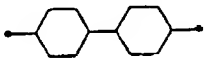
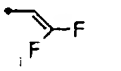
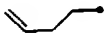
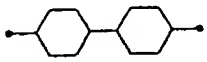
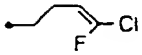
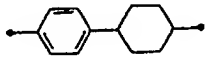
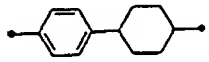
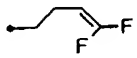
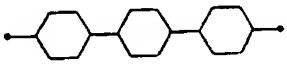
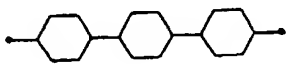
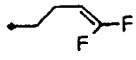
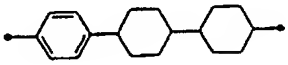
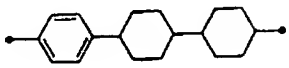
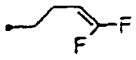
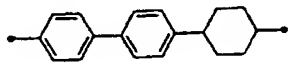
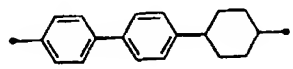
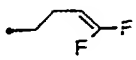
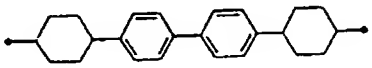
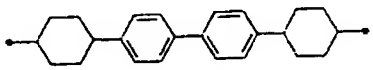
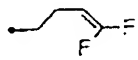
^{1}H-NMR: δ :(ppm): 0.40~2.55 (m, 28H), 4.10 (d, d, t, 1H, J_{H-F}=25.3, J=7.7, J_{H-F}=3.1), 4.80~5.20 (m, 2H), 5.82 (d, d, t, 1H, J_{H-F}=17.1, 9.9, J=6.7).

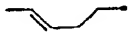
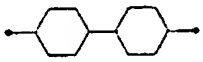
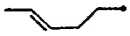
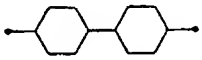
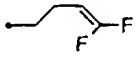
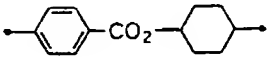
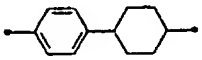
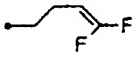
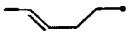
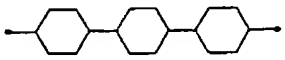
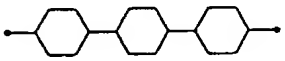
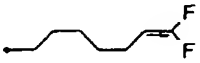
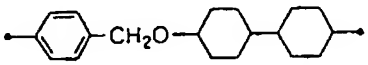
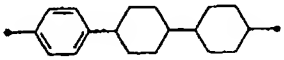
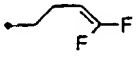
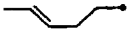
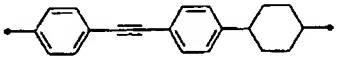
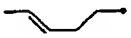
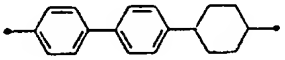
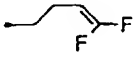
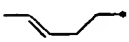
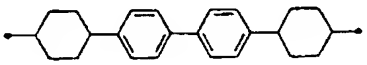
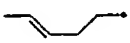
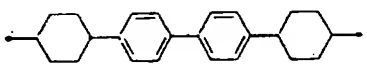
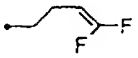
MS:m/e=310(M^+), 253, 239, 137, 95, 81, 67.

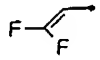
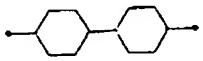
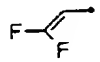
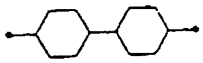
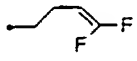
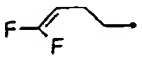
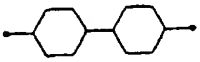
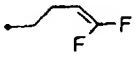
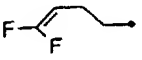
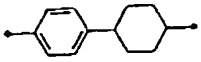
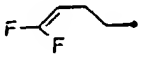
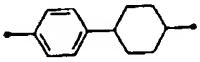
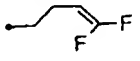
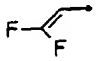
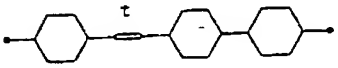
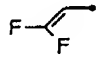
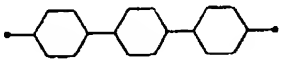
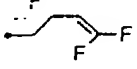
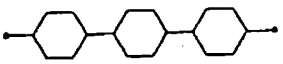
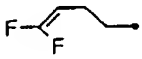
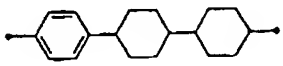
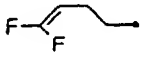
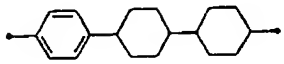
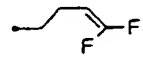
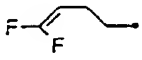
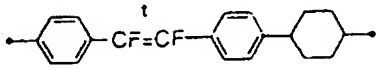
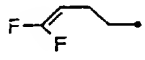
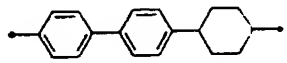
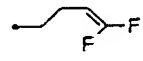
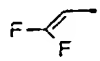
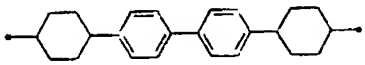
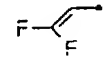
The following compounds can be prepared according to the methods of Examples 1 to 5.

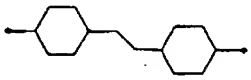
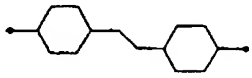
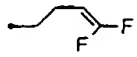
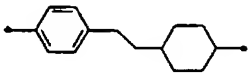
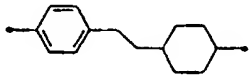
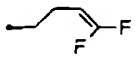
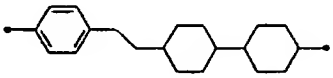
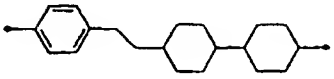
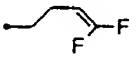
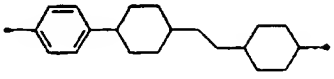
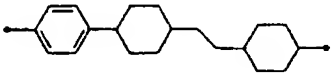
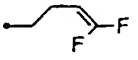
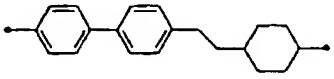
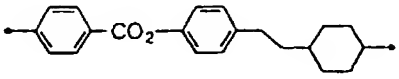
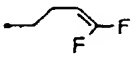
	Q_1-$(CH_2)_l$-$C(Q_2)$=$(CH_2)_m$	-$(A_1$-$Z_1)_p$-$(A_2$-$Z_2)_q$-A_3-Z_3-A_4-	-$(CH_2)_n$-$C(Q_3)$=Q_4
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			

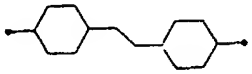
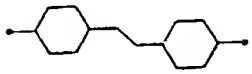
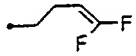
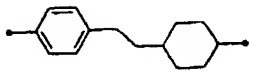
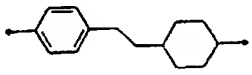
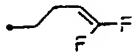
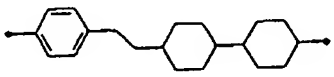
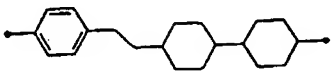
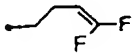
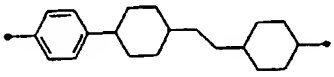
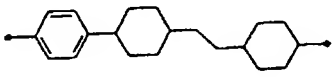
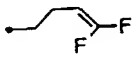
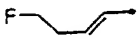
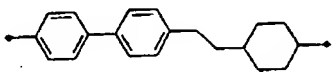
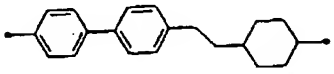
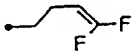
	O_1-$(CH_2)_l$-$C(O_2)$=$(CH_2)_m$	-$(A_1$-$Z_1)_p$-$(A_2$-$Z_2)_q$-A_3-Z_3-A_4-	-$(CH_2)_n$-$C(O_3)$=O_4
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			

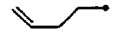
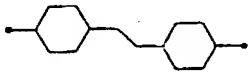
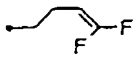
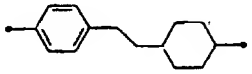
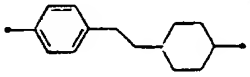
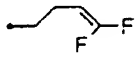
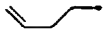
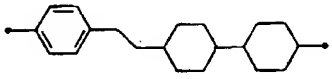
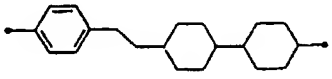
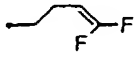
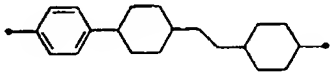
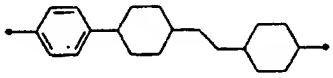
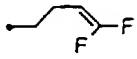
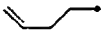
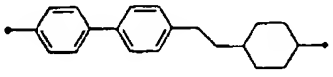
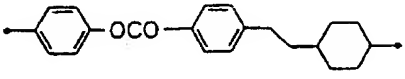
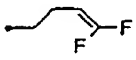
	Q_1-$(CH_2)_l$-$C(Q_2)$=$(CH_2)_m$	-$(A_1$-$Z_1)_p$-$(A_2$-$Z_2)_q$-A_3-Z_3-A_4-	-$(CH_2)_n$-$C(Q_3)$=Q_4	
25				Cr -7.1 S -4.9 N 49.7 Iso
26				
27				
28				
29				Cr 36.5 S 205.8 N 236.2 Iso
30				
31				
32				
33				
34				
35				
36				

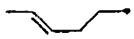
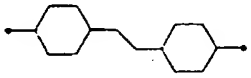
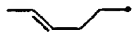
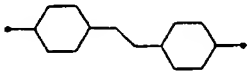
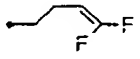
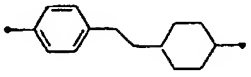
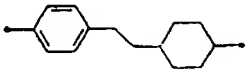
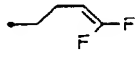
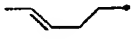
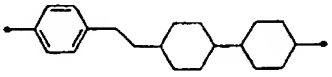
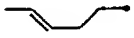
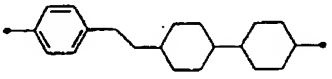
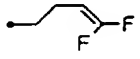
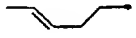
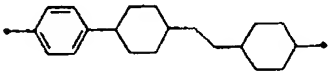
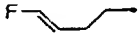
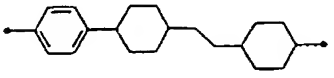
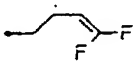
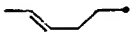
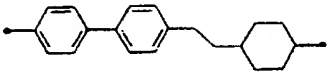
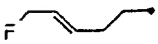
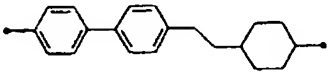
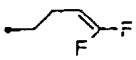
	$Q_1\text{-}(CH_2)_l\text{-}C(Q_2)=CH\text{-}(CH_2)_m$	$(A_1\text{-}Z_1)_p\text{-}(A_2\text{-}Z_2)_q\text{-}A_3\text{-}Z_3\text{-}A_4$	$(CH_2)_n\text{-}C(Q_3)=CH\text{-}Q_4$
37			
38			
39			
40			
41			
42			
43			
44			
45			
46			
47			
48			

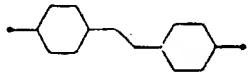
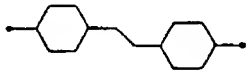
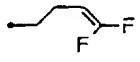
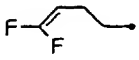
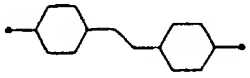
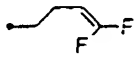
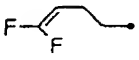
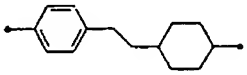
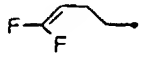
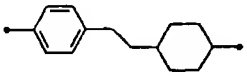
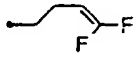
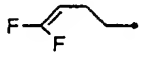
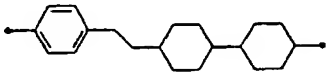
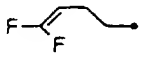
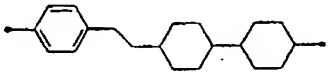
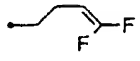
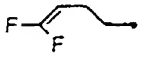
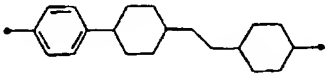
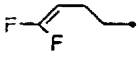
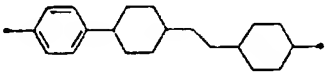
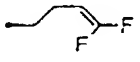
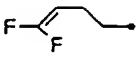
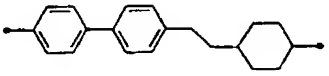
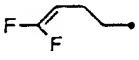
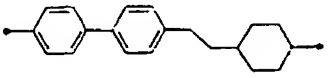
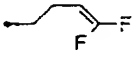
	Q_1-$(CH_2)_l$-$C(Q_2)$=$(CH_2)_m$	-$(A_1$-$Z_1)_p$-$(A_2$-$Z_2)_q$-A_3-Z_3-A_4-	-$(CH_2)_n$-$C(Q_3)$=C_4
49			
50			
51			
52			
53			
54			
55			
56			
57			
58			
59			
60			
61			
62			
63			

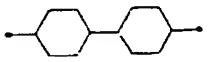
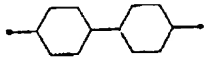
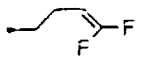
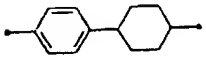
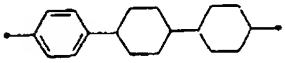
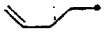
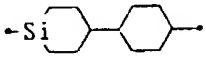
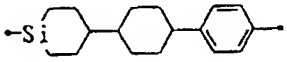
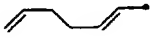
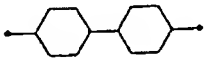
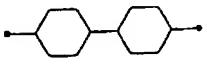
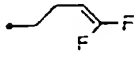
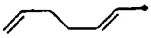
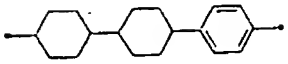
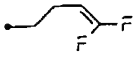
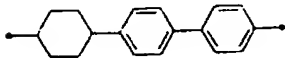
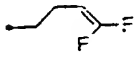
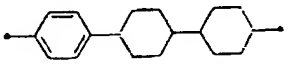
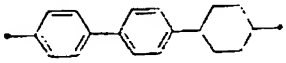
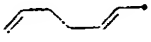
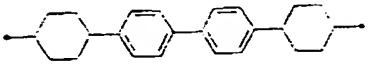
	$Q_1\text{-}(CH_2)$ — Q_2 / $(CH_2)_m$	$-(A_1\text{-}Z_1)_p-(A_2\text{-}Z_2)_q-A_3\text{-}Z_3\text{-}A_4-$	$-(CH_2)_n$ — Q_3 — Q_4
64			
65			
66			
67			
68			
69			
70			
71			
72			
73			

	$Q_1\text{-}(CH_2)_l\text{-}\underset{}{\overset{Q_2}{C}}\text{=}\underset{}{C}\text{-}(CH_2)_m\rightarrow$	$\leftarrow(A_1\text{-}Z_1)_p\text{-}(A_2\text{-}Z_2)_q\text{-}A_3\text{-}Z_3\text{-}A_4\rightarrow$	$\leftarrow(CH_2)_n\text{-}\underset{Q_3}{C}\text{=}C\text{-}Q_4$
74			
75			
76			
77			
78			
79			
80			
81			
82			
83			

	$Q_1\text{-}(CH_2)_l\text{-}C(Q_2)=CH\text{-}(CH_2)_m$	$(A_1\text{-}Z_1)_p\text{-}(A_2\text{-}Z_2)_q\text{-}A_3\text{-}Z_3\text{-}A_4$	$(CH_2)_n\text{-}C(Q_3)=CH\text{-}Q_4$
84			
85			
86			
87			
88			
89			
90			
91			
92			
93			

	Q_1-$(CH_2)_l$-$\overset{Q_2}{C}$=$(CH_2)_m$	-$(A_1$-$Z_1)_p$-$(A_2$-$Z_2)_q$-A_3-Z_3-A_4-	-$(CH_2)_n$-$\overset{Q_3}{C}$=C_4
94			
95			
96			
97			
98			
99			
100			
101			
102			
103			

	$Q_1\text{-}(CH_2)_l\text{-}C(Q_2)=CH\text{-}(CH_2)_m$	$(A_1\text{-}Z_1)_p\text{-}(A_2\text{-}Z_2)_q\text{-}A_3\text{-}Z_3\text{-}A_4$	$(CH_2)_n\text{-}C(Q_3)=CH\text{-}Q_4$
104			
105			
106			
107			
108			
109			
110			
111			
112			
113			
114			

	Q_1-$(CH_2)_l$-$\overset{Q_2}{C}$=$(CH_2)_m$	-$(A_1$-$Z_1)_p$-$(A_2$-$Z_2)_q$-A_3-Z_3-A_4-	-$(CH_2)_n$-$\overset{Q_3}{C}$=C_4	
115				Cr -7.0 S_B 49.0 N 69.0 iso
116				
117				
118				
119				
120				
121				
122				
123				
124				
125				
126				
127				

Effects of the Invention

Compounds of the invention, that is, bicyclic to tetracyclic type compounds having an alkenyl group optionally substituted by (a) halogen(s) and an alkenyl group substituted by (a) halogen(s) simultaneously at both terminals of molecule show the following characteristics:

1) They have a wide liquid crystal Phase temperature range in spite of containing an alkenyl group. For example, the compound described in Toku-Kai-Hei 1-175947, trans-4-(trans-4-propylcyclohexyl)-1-(2,2-difluoro-1-ethenyl)cyclohexane, has a liquid crystal phase temperature range of about 47℃, wherein a temperature range of SB phase being about 40℃. In contrast to it, the compound of the present invention, 1-(2,2-difluoroethenyl)-trans-4-(trans-4-(3-butenyl)cyclohexyl) cyclohexane, does not make an appearance of SB phase and has a liquid crystal phase temperature range of about 56℃, which being much improved.

2) There are obtained decrease in a threshold voltage and improvement in a response speed due to a low viscosity.

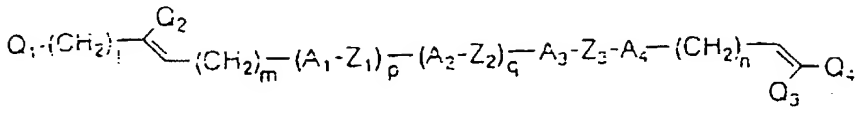
3) Nematic liquid crystal composition can be prepared without any deposition of crystals and any appearance of smectic phase at an extremely low temperature.

4) A high contrast can be obtained due to improvement in an elastic constant ratio K_{33}/K_{11}.

As well as, they are stable against external enveironments and also they can provide novel liquid crystal compositions and liquid crystal display devices by which enlargement of the used temperature range, a driving property at a low voltage, a high speed response and a high contrast can be realized.

C L A I M S

1. A liquid crystalline compound expressed by the general formula (1)



(1)

wherein, A_1, A_2, A_3 and A_4 denote each independently trans-1,4-cyclohexylene group, trans-1,4-silacyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on 6-membered ring(s) are optionaly substituted with (a) halogen atom(s), pyrimidine-2,5-diyl group, 1,3-dioxane-2,5-diyl group, tetrahydropyran-2,5-diyl group, 1,3-dithiane-2,5-diyl group or tetrahydrothiopyran-2,5-diyl group; Z_1, Z_2 and Z_3 denote each independently $-(CH_2)_2-$, $-(CH_2)_4-$, $-CH=CH-$, $-C\equiv C-$, $-COO-$, $-OCO-$, $-CH_2O-$, $-OCH_2-$, $-CF=CF-$ or a covalent bond; Q_1 and Q_2 denote each independently H, F, Cl, Br or an alkenyl group having 2 to 5 carbon atoms; Q_3 and Q_4 denote each independently H, F, Cl or Br; l, m and n denote each independently an integer of 0 to 5; and p and q denote each independently an integer of 0 or 1.

2. A liquid crystalline compound according to Claim 1, wherin p, q and n are 0; Q_3 and Q_4 are F; Z_3 is a covalent bond; and A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

3. A liquid crystalline compound according to Claim 1, wherein p and q are 0; Q_3 and Q_4 are F; Z_3 is a covalent bond; and A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

4. A liquid crystalline compound according to Caim 1, wherein p and n are 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; and A_2, A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

5. A liquid crystalline compound according to Claim 1, wherein p is 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; and A_2, A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

6. A liquid crystalline compound according to Claim 1, wherein p and n are 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; A_2 is 1, 4-phenylene group; and A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

7. A liquid crystalline compound according to Claim 1, wherein p is 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; A_2 is 1, 4-phenylene group; and A_3 and A_4 are trans-1,4-cyclohexylene groups in the general formula (1).

8. A liquid crystalline compound according to Claim 1, wherein p and n are 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; A_2 and A_3 are 1, 4-phenylene groups, and A_4 is trans-1,4-cyclohexylene group in the general formula (1).

9. A liquid crystalline compound according to Claim 1, wherein p is 0; q is 1; Q_3 and Q_4 are F; Z_2 and Z_3 are covalent bonds; A_2 and A_3 are 1, 4-phenylene groups; and A_4 is trans-1,4-cyclohexylene group in the general formula (1).

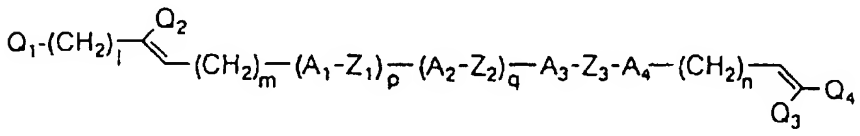
10. A liquid crystalline compound according to Claim 1, wherein p and q are 1; n is 0; Q_3 and Q_4 are F; Z_1, Z_2 and Z_3 are covalent bonds; A_1 and A_4 are trans-1,4-cyclohexylene groups;

and A_2 and A_3 are 1,4-phenylene groups in the general formula (1).

11. A liquid crystalline compound according to Claim 1, wherein p and q are 1; Q_3 and Q_4 are F; Z_1, Z_2 and Z_3 are covalent bonds; A_1 and A_4 are trans-1,4-cyclohexylene groups, and A_2 and A_3 are 1, 4-phenylene groups in the general formula (1).

12. A liquid crystal composition consisting of two or more than two components and a display device using the said composition, wherein at least one liquid compound(s) according to any of Claim 1 to 11 is(are) contained.

13. A liquid crystal composition characterized in that at least one liquid crystalline compound(s) expressed by the general formula (1)

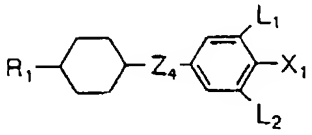


(1)

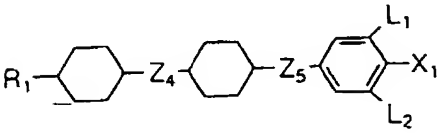
wherein, A_1, A_2, A_3 and A_4 denote each independently trans-1,4-cyclohexylene group, trans-1,4-silacyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on 6-membered ring(s) are optionaly substituted with (a) halogen atom(s), pyrimidine-2,5-diyl group, 1,3-dioxane-2,5-diyl group, tetrahydropyran-2,5-diyl group, 1,3-dithiane-2,5-diyl group or tetrahydrothiopyran-2,5-diyl group; Z_1, Z_2 and Z_3 denote each independently $-(CH_2)_2-$, $-(CH_2)_4-$, $-CH=CH-$, $-C\equiv C-$, $-COO-$, $-OCO-$, $-CH_2O-$, $-OCH_2-$, $-CF=CF-$ or a covalent bond; Q_1 and Q_2 denote each independently H, F, Cl, Br or an alkenyl group having 2 to 5 carbon atoms; Q_3 and Q_4 denote each independently H, F, Cl or

Br; l, m and n denote each independently an integer of 0 to 5; and p and q denote each independently an integer of 0 or 1, is(are) contained as the first component, and

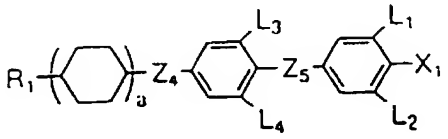
that at least one compound(s) selected from the group consisting of the general formulae (2), (3) and (4)



(2)



(3)

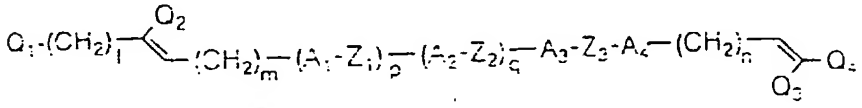


(4)

wherein, R_1 denotes an alkyl group having 1 to 10 carbon atoms; X_1 denotes F, Cl, OCF_3, OCF_2H, CF_3, CF_2H or CFH_2; L_1, L_2, L_3 and L_4 denote each independently H or F; Z_4 and Z_5 denote each independently $-(CH_2)_2-$, -CH=CH- or a covalent bond; and a denotes 1 or 2,

is(are) contained as the second component.

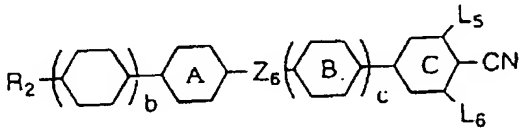
14. A liquid crystal composition characterized in that at least one liquid crystalline compound(s) expressed by the general formula (1)



(1)

wherein, A_1, A_2, A_3 and A_4 denote each independently trans-1,4-cyclohexylene group, trans-1,4-silacyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on 6-membered ring(s) are optionaly substituted with (a) halogen atom(s), pyrimidine-2,5-diyl group, 1,3-dioxane-2,5-diyl group, tetrahydropyran-2,5-diyl group, 1,3-dithiane-2,5-diyl group or tetrahydrothiopyran-2,5-diyl group; Z_1, Z_2 and Z_3 denote each independently $-(CH_2)_2-$, $-(CH_2)_4-$, $-CH=CH-$, $-C\equiv C-$, $-COO-$, $-OCO-$, $-CH_2O-$, $-OCH_2-$, $-CF=CF-$ or a covalent bond; Q_1 and Q_2 denote each independently H, F, Cl, Br or an alkenyl group having 2 to 5 carbon atoms; Q_3 and Q_4 denote each independently H, F, Cl or Br; l, m and n denote each independently an integer of 0 to 5; and p and q denote each independently an integer of 0 or 1, is(are) contained as the first component, and

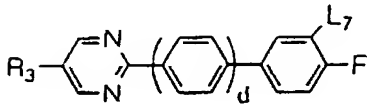
that at least one compound(s) selected from the group consisting of the general formulae (5), (6), (7), (8) and (9)



(5)

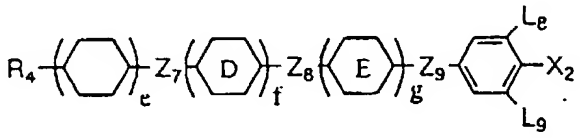
wherein, R_2 denotes F, an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in the said alkyl group or alkenyl group may be substituted with (an) oxygen atom(s) (-O-) but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring A denotes trans-1,4-cyclohexylene group, 1,4-phenylene group, pyrimidine-2,5-diyl

group or 1,3-dioxane-2,5-diyl group; ring B denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring C denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_6 denotes $-(CH_2)_2-$, -COO- or a covalent bond; L_5 and L_6 denote each independently H or F; and b and c denote each independently 0 or 1,



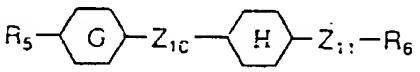
(6)

wherein, R_3 denotes an alkyl group having 1 to 10 carbon atoms; L_7 denotes H or F; and d denotes 0 or 1,



(7)

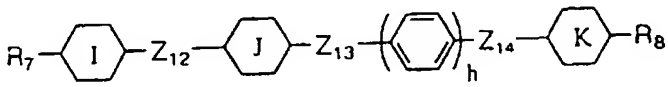
wherein, R_4 denotes an alkyl group having 1 to 10 carbon atoms; ring D and ring E denote each independently trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_7 and Z_8 denote each independently -COO- or a covalent bond; Z_9 denotes -COO- or $-C\equiv C-$; L_8 and L_9 denote each independently H or F; X_2 denotes F, OCF_3, OCF_2H, CF_3, CF_2H or CFH_2; and e, f and g denote each independently 0 or 1,



(8)

wherein, R_5 and R_6 denote each independently an alkyl group having 1 to 10 carbon atom(s) or an alkenyl group having 2 to 10

carbon atoms, in which optional methylene group(s) ($-CH_2-$) in either cases may be substituted with (an) oxygen atom(s: (-O-) but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring G denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring H denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_{10} denotes $-C\equiv C-$, $-COO-$, $-(CH_2)_2-$, $-CH=CH-C\equiv C-$ or a covalent bond; and Z_{11} denotes $-COO-$ or a covalent bond,

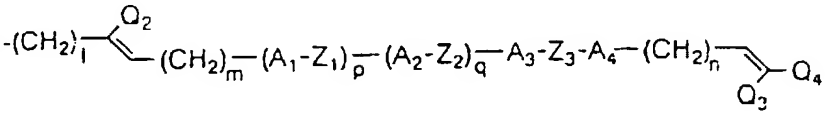


(9)

wherein, R_7 and R_8 denote each independently an alkyl group having 1 to 10 carbon atom(s) or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in either cases may be substituted with (an) oxygen atom(s) (-O-) but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring I denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring J denotes trans-1,4-cyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on ring may be substituted with F, or pyrimidine-2,5-diyl group; ring K denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_{12} and Z_{14} denote each independently $-COO-$, $-(CH_2)_2-$ or a covalent bond; Z_{13} denotes $-CH=CH-$, $-C\equiv C-$, $-COO-$ or a covalent bond; and h denotes 0 or 1,

is(are) contained as the second component.

15. A liquid crystal composition and a liquid crystal display device using the said comosition characterized in that at least one liquid crystalline compound(s) expressed by the general formula (1)

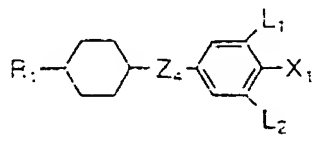


(1)

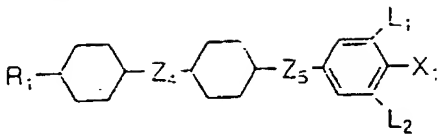
wherein, A_1, A_2, A_3 and A_4 denote each independently trans-1,4-cyclohexylene group, trans-1,4-silacyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on 6-membered ring(s) are optionaly substituted with (a) halogen atom(s), pyrimidine-2,5-diyl group, 1,3-dioxane-2,5-diyl group, tetrahydropyran-2,5-diyl group, 1,3-dithiane-2,5-diyl group or tetrahydrothiopyran-2,5-diyl group; Z_1, Z_2 and Z_3 denote each independently $-(CH_2)_2-$, $-(CH_2)_4-$, $-CH=CH-$, $-C\equiv C-$, $-COO-$, $-OCO-$, $-CH_2O-$, $-OCH_2-$, $-CF=CF-$ or a covalent bond; Q_1 and Q_2 denote each independently H, F, Cl, Br or an alkenyl group having 2 to 5 carbon atoms; Q_3 and Q_4 denote each independently H, F, Cl or Br; l, m and n denote each independently an integer of 0 to 5; and p and q denote each independently an integer of 0 or 1,

is(are) contained as the first component,

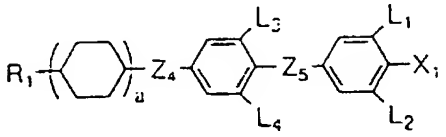
that at least one compound(s) selected from the group consisting of the general formulae (2), (3) and (4)



(2)



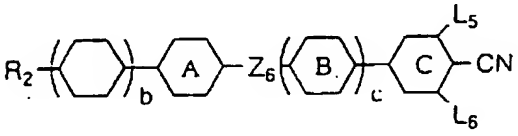
(3)



(4)

wherein, R_1 denotes an alkyl group having 1 to 10 carbon atoms; X_1 denotes F, Cl, OCF_3, OCF_2H, CF_3, CF_2H or CFH_2; L_1, L_2, L_3 and L_4 denote each independently H or F; Z_4 and Z_5 denote each independently $-(CH_2)_2-$, $-CH=CH-$ or a covalent bond; and a denotes 1 or 2,

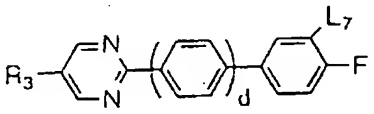
is(are) contained as one part of the second component, and that at least one compound(s) selected from the group consisting of the general formulae (5), (6), (7), (8) and (9)



(5)

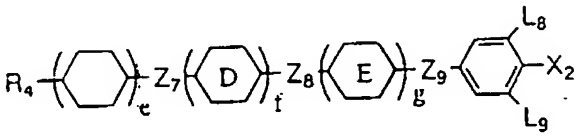
wherein, R_2 denotes F, an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in the said alkyl group or alkenyl group may be substituted with (an) oxygen atom(s) (-O-) out two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring A denotes trans-1,4-cyclohexylene group, 1,4-phenylene group, pyrimidine-2,5-diyl group or 1,3-dioxane-2,5-diyl group; ring B denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl

group; ring C denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_6 denotes $-(CH_2)_2-$, -COO- or a covalent bond; L_5 and L_6 denote each independently H or F; and b and c denote each independently 0 or 1,



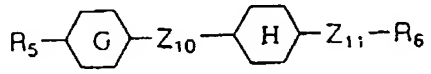
(6)

wherein, R_3 denotes an alkyl group having 1 to 10 carbon atoms; L_7 denotes H or F; and d denotes 0 or 1,



(7)

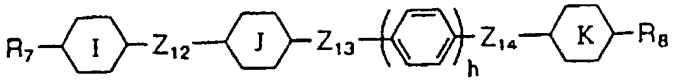
wherein, R_4 denotes an alkyl group having 1 to 10 carbon atoms; ring D and ring E denote each independently trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_7 and Z_8 denote each independently -COO- or a covalent bond; Z_9 denotes -COO- or $-C\equiv C-$; L_8 and L_9 denote each independently H or F; X_2 denotes F, OCF_3, OCF_2H, CF_3, CF_2H or CFH_2; and e, f and g denote each independently 0 or 1,



(8)

wherein, R_5 and R_6 denote each independently an alkyl group having 1 to 10 carbon atom(s) or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in

either cases may be substituted with (an) oxygen atom(s) (-O-) but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring G denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring H denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_{10} denotes -C≡C-, -COO-, $-(CH_2)_2-$, -CH=CH-C≡C- or a covalent bond; and Z_{11} denotes -COO- or a covalent bond,



(9)

wherein, R_7 and R_8 denote each independently an alkyl group having 1 to 10 carbon atom(s) or an alkenyl group having 2 to 10 carbon atoms, in which optional methylene group(s) ($-CH_2-$) in either cases may be substituted with (an) oxygen atom(s) (-O-) but two or more than two methylene groups may not be substituted with oxygen atoms consecutively; ring I denotes trans-1,4-cyclohexylene group, 1,4-phenylene group or pyrimidine-2,5-diyl group; ring J denotes trans-1,4-cyclohexylene group, 1,4-phenylene group in which one or more than one hydrogen atom(s) on ring may be substituted with F, or pyrimidine-2,5-diyl group; ring K denotes trans-1,4-cyclohexylene group or 1,4-phenylene group; Z_{12} and Z_{14} denote each independently -COO-, $-(CH_2)_2-$ or a covalent bond; Z_{13} denotes -CH=CH-, -C≡C-, -COO- or a covalent bond; and h denotes 0 or 1,

is(are) contained as the second component.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 97/00700

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C22/00 C09K19/30 C09K19/40 C07C25/24 C07C69/76
C07C43/192 C07F7/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C C09K C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 07234 A (F. HOFFMANN-LA ROCHE AG) 15 April 1993 see page 28, lines 19-28, page 29, lines 18-26, page 38, line 9, page 40, line 7, page 43, line 41 to page 44, line 8, page 44, lines 25-34, page 45, lines 9-18, etc ---	1-15
X	WO 92 21734 A (MERCK PATENT GMBH) 10 December 1992 see page 92, line 18, page 93, line 6; claims 1-11 ---	1-15
X	EP 0 168 683 A (F. HOFFMANN-LA ROCHE & CO.) 22 January 1986 cited in the application see example 23 --- -/--	1-15

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 May 1997	10 -06- 1997
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer Beslier, L

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 97/00700

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 30723 A (MERCK PATENT GMBH) 16 November 1995 see pages 7-9, pages 76-77; claims 9,14,18	1-15
X	EP 0 325 796 A (CHISSO CORP.) 2 August 1989 cited in the application see claims 1-16	1-15
X	DE 44 26 799 A (MERCK PATENT GMBH) 9 February 1995 see claim 4	1-15
P,X	EP 0 747 336 A (CHISSO CORP.) 11 December 1996 see page 41, compound 33; examples 5,6 8; pages 67-72; claims 1-10	1-15
P,X	WO 96 37451 A (CHISSO CORP.) 28 November 1996 see page 95, compound 25; claims 1-15	1-15
P,X	EP 0 750 028 A (CHISSO CORP.) 27 December 1996 see pages 12-14, page 21, pages 73-80, claims 1-15	1-15

1

INTERNATIONAL SEARCH REPORT

.nformation on patent family members

Inte tional Application No
PCT/JP 97/00700

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9307234 A	15-04-93	DE 69208351 D	28-03-96
		DE 69208351 T	13-06-96
		EP 0559860 A	15-09-93
		JP 6503362 T	14-04-94
		US 5364556 A	15-11-94
WO 9221734 A	10-12-92	AU 1878092 A	08-01-93
		CA 2088771 A	06-12-92
		DE 4217248 A	28-01-93
		DE 59207843 D	20-02-97
		EP 0541793 A	19-05-93
		JP 6500343 T	13-01-94
		US 5403512 A	04-04-95
EP 168683 A	22-01-86	HK 91892 A	27-11-92
		JP 7002653 B	18-01-95
		JP 61083136 A	26-04-86
		US 5238602 A	24-08-93
WO 9530723 A	16-11-95	DE 4416455 A	16-11-95
		DE 4434851 A	04-04-96
		DE 4441963 A	16-11-95
		DE 4442842 A	05-06-96
		DE 19511632 A	02-10-96
		AU 2526395 A	29-11-95
		EP 0759058 A	26-02-97
EP 325796 A	02-08-89	JP 1308239 A	12-12-89
		JP 2525224 B	14-08-96
		JP 1175947 A	12-07-89
		JP 2516038 B	10-07-96
		CA 1336441 A	25-07-95
		DE 3869114 A	16-04-92
		US 4877548 A	31-10-89
DE 4426799 A	09-02-95	JP 7053432 A	28-02-95
EP 747336 A	11-12-96	JP 9052851 A	25-02-97
WO 9637451 A	28-11-96	JP 8325173 A	10-12-96

INTERNATIONAL SEARCH REPORT

nformation on patent family members

Inter ional Application No
PC:/JP 97/00700

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 750028 A	27-12-96	NONE	